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DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY





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MODEL****I****is for Important Improvement
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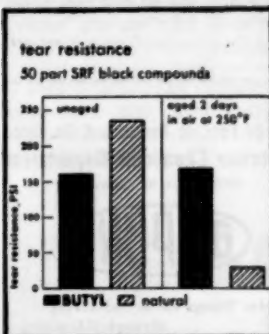
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MBT
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MBTS Grains
NA-22
Permalux
Polyac Pellets
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Telone A
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Thiuram E Grains
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Thiuram M Grains
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Hylone® MP
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Hylone® TM
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RPA No. 3
RPA No. 3 Concentrated
RPA No. 6
RR-10

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Neozone C
Neozone D
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NBC—Inhibits weather and ozone cracking of SBR compounds

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RETARDER W
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Unicel NDX
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	C-P-B®	G-M-F	
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D-B-A Accelerator

ANTIOXIDANTS

Discoloring	Nondiscoloring	Semi-nondiscoloring	Antiozonants
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Flexamine G			
V-G-B®			

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Celogen® Celogen-80 Celogen-AZ®

SUNPROOFING WAXES

Sunproof® Regular Sunproof® Improved Sunproof® Jr.
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MISCELLANEOUS SPECIAL PRODUCTS

BWH-I — mixture of oils
DDM — dodecyl mercaptan
LAUREX® — zinc laurate
PROCESS STIFFENER #710 —
26.4% hydrazine salt and 73.6%
inert mineral filler

THIOSTOP K — 40% aqueous
solution of potassium dimethyl
dithiocarbamate

THIOSTOP N — 35% aqueous
solution of sodium dimethyl
dithiocarbamate

TONOX — p,p'-diaminodiphenylmethane

RETARDERS

RETARDER E-S-E-N RETARDER J

*available in Naugat form



Naugatuck Chemical

Division of United States Rubber Company

71 R Elm Street

Naugatuck, Connecticut



Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latex
CANADA: Naugatuck Chemicals Division, Dominion Rubber Co., Ltd., Elmira, Ontario • CABLE: Rubberport, N.Y.

Naugatuck PARACRILS

Industry's most complete range of
oil-resistant nitrile rubbers
plus weather-resistant OZO

PARACRIL IS-80—Moderate oil resistance, excellent low-temperature flexibility.

PARACRIL AJ—Moderate oil resistance, easy processing, very good low-temperature performance.

PARACRIL ALT*—Low-temperature polymerized, high physicals, excellent low-temperature properties.

PARACRIL B—Good oil resistance, moderate low-temperature flexibility.

PARACRIL BJ—Like B but lower Mooney for easy processing.

PARACRIL BLT*—Low-temperature polymerized; high physicals, excellent processing.

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*New Cold types



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these skate wheels play a dual role

Hard on the outer edge for longer wear; softer on the inner edge for better traction, less noise. The two shades of color you see in these roller skate wheels show how two different Hycar nitrile rubber compounds are used to serve different needs in the same product.

The outer $\frac{1}{8}$ " of each wheel is a phenolic compound made with extra-tough Hycar rubber for better abrasion resistance. The inner portion of the wheel is made from a softer Hycar phenolic compound. The two are inseparably bonded during molding.

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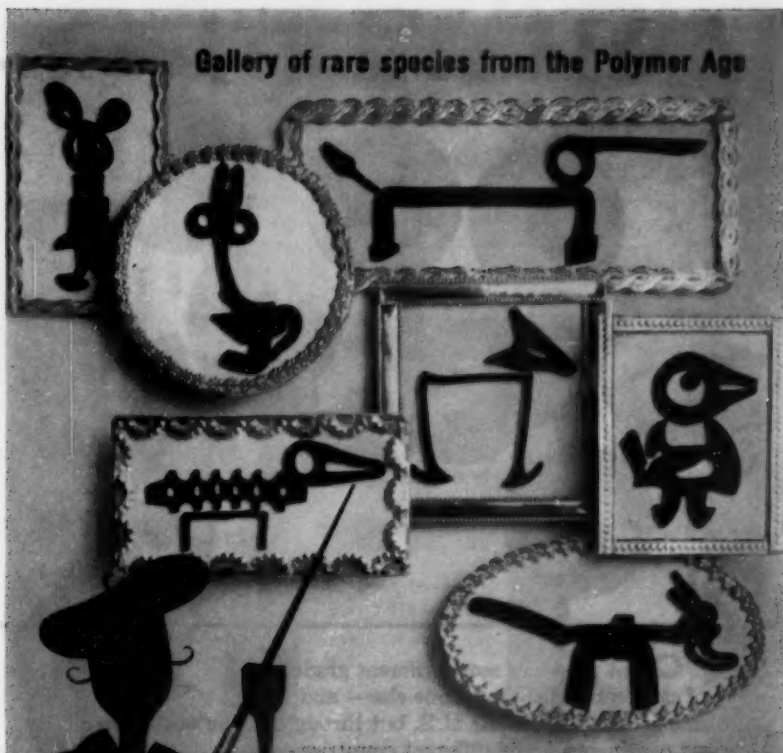
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Rubber and Latex

B.F. Goodrich Chemical Company
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*See our catalog in Sweet's Product Design File.



GEON vinyls • HYCAR rubber and latex • GOOD-RITE chemicals and plasticizers



Cross sections of extrusions courtesy Bowling Green Rubber Co., Paris, Tenn.

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Cabot produces more different grades of carbon black than anyone else — and sells more — not only in the U.S. but throughout the world. On all six continents. In 58 different countries.

Cabot has more production facilities — abroad — than anyone else. Ships from more countries. Sells in more currencies. And Cabot is continually establishing new plants.

That's why Cabot can serve your carbon black needs better than anyone else — internationally.

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FURNACE BLACKS:	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Vulcan XC-72 ECF	Vulcan SC SCF
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	Sterling 5 SRP	Sterling NS SRP	Pallotex SRP	Pallotex NS SRP	Sterling R SRP
THERMAL BLACKS:	Sterling FT	Sterling MT	Sterling MT-NS	Sterling FT-PF	Sterling MT-PF
	Sterling MT-NS-PF				
REGAL BLACKS:	Regal 300	Regal 600	Regal SRP		



reduce moisture absorption with Columbia-Southern Hi-Sil®

The degree of water absorption is extremely low when you compound with Hi-Sil, a high quality white reinforcing pigment. Your products exhibit less swelling, longer life. That's why so many rubber goods manufacturers specify Hi-Sil for industrial and household products that come in contact with water or a moist environment.

Have you seen Columbia-Southern's new report on the comparative water absorption of various rubber compounds? If not, write for a copy—at no obligation.

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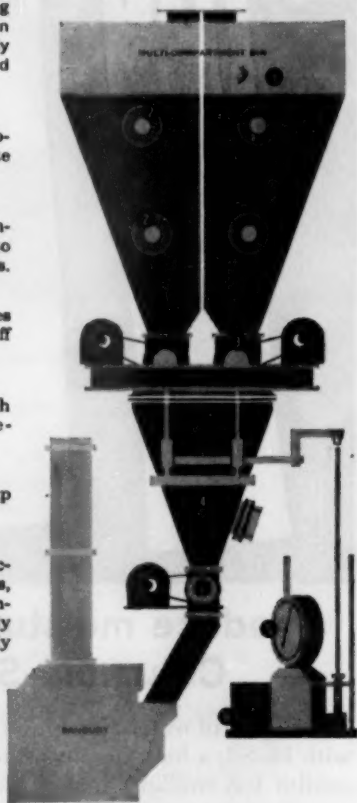
KENNEDY

CARBON BLACK PROPORTIONING SYSTEM

for cleanliness • accuracy • quality control

This complete, self-contained carbon black feeding and weighing system accurately proportions carbon black additions to Banburys. It eliminates costly manual handling, unsightly housekeeping and batch-to-batch inaccuracies.

- ① **BINS** . . . KENNEDY bins are designed and fabricated for free flow without bridging. Separate bins are provided for each type of black.
- ② **LEVEL CONTROL** . . . High- and low-level controls actuate the carbon black conveyors to the bins, maintaining a steady supply of blacks.
- ③ **FEEDERS** . . . Proven KENNEDY design provides uniform "Stream-in-air" for accurate cut-off and close weighing tolerances.
- ④ **WEIGH HOPPER** . . . The design of the weigh hopper assures complete cleanout between batches.
- ⑤ **SCALE** . . . The scale automatically weighs up to four blacks in sequence.
- ⑥ **CONTROL CENTER** . . . After manual preselection of the feed sequence and black weights, this center automatically controls the entire feed operation. Cycle is automatically repeated. Batch weights are accurately duplicated.
- ⑦ **ROTARY DISCHARGE GATE** . . . When actuated by the control center, the weigh hopper gate discharges the weighed blacks into the Banbury at a rate which can be set to meet mixer cycle requirements.



KENNEDY Carbon Black Systems in rubber plants throughout this country and abroad are doing an outstanding job of producing more uniform batches under cleaner working conditions without manual handling.

To get the best out of your existing equipment, install a KENNEDY Carbon Black Proportioning System. Ask a KENNEDY Engineer to show you how this package can improve your carbon black operation. There is no obligation.



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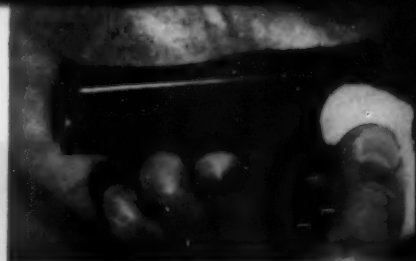
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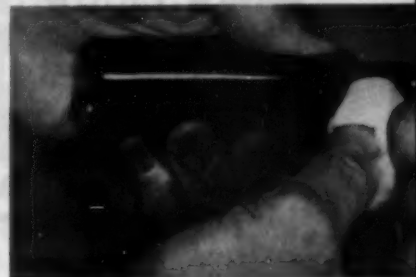
HOW SULFASAN R ANSWERS YOUR CURING NEEDS IN NONBLOOMING, SCORCH-FREE, HEAT-RESISTANT COMPOUNDS OF SBR AND NATURAL RUBBER

Results with scores of different stocks compounded with SULFASAN R, powerful organic-type vulcanizing agent, all show increased heat resistance, greatly reduced scorch... and no bloom even after months of aging.

Economical SULFASAN R frequently trims costs, too... substantially reduces the total amount of curing agents required. Only 1 pph of SULFASAN R plus a small amount of THIURAD (tetramethylthiuram disulfide) achieves good results with most SBR and natural compounds.



Without SULFASAN R—Stock Blooms Readily



With SULFASAN R—No Bloom at All

SPECIFICATION: Withstand 70 hours @ 250° F. and 24 hours @ 325° F. in air oven without cracking when flexed 180°

COMPOUNDS	A	B	C
SBR 1500	100	100	100
Black	75	75	75
Zinc Oxide	5	5	5
Stearic Acid	1	1	1
Santoflex 75	1	1	1
Flectol H	2	2	2
Santocure	2	2	2
THIURAD	3.5	1.25	1.25
SULFASAN R	—	1.25	0.75
CURING AGENT COST	\$3.99	\$3.36	\$2.59
TYPICAL RESULTS			
Mooney Scorch (Large Rotor @ 250° F.)			
Minutes for 10 point rise	8	11½	13
Unaged			
Tensile, psi.	1860	2130	2070
Elongation, %	480	440	515
Hardness	60	60	59
Aged 70 Hours @ 250° F.			
Tensile, psi.	2100	2260	2210
Elongation, %	260	235	290
Hardness	69	69	68
BLOOM	Immediately	None in 9 months	None in 9 months

SULFASAN R gives improved aging because of low sulfur content... won't stain or discolor white rubbers. SULFASAN R disperses readily. Works well for butyl and Buna-N as well as SBR and natural rubbers... especially when used with SANTOCURE and other sulfenamide accelerators.

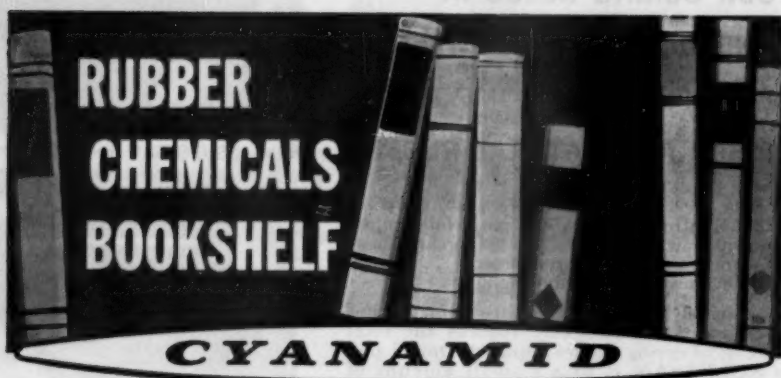
For further information about unique SULFASAN R, or help with a specific compounding project, write or phone, today.

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CHEMICAL
COMPANY**

Rubber Chemicals Dept.
Akron 11, Ohio
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The need of compounders and development chemists for dependable information on commercial rubber chemicals is appreciated by the Rubber Chemicals Department at Cyanamid. The literature listed below has been prepared to meet the critical requirements of rubber manufacturers.

ANTIOXIDANT 2246®

The use of this powerful and non-discoloring antioxidant in various formulas is described. (*Bull. No. 815-B*)

ANTIOXIDANT 425®

Contains information on the use of this premium grade antioxidant in white rubber stocks where minimum discoloration is paramount. (*Bull. No. 840*)

THIAZOLE ACCELERATORS—MBT and MBTS
Formulating data as well as compounding characteristics are shown.

(*Bull. No. 839*)

CYDAC* ACCELERATOR FLAKED

Describes and gives data on this well-known accelerator (N-cyclohexyl benzothiazole-2-sulfenamide) now available in flaked form.

DELAYED-ACTION ACCELERATORS

NOBS® No. 1; NOBS® Special

Contains compounding information and performance graphs on these two delayed-action accelerators.

(*Bull. No. 836*)

DIBS® DELAYED-ACTION ACCELERATOR

Describes this new extra-delayed-action accelerator that is especially suitable for higher and more critical processing temperatures. (*Bull. No. 850*)

GUANIDINES DPG and DOTG

Describes these products as primary accelerators and as activators with thiazoles. (*Bull. No. 848*)

2-MT ACCELERATOR

Gives data on this fast-curing accelerator for certain natural GR-S stocks and for latex.

RETARDER PD—AN ANTI-SCORCH AGENT

Discusses the use of this anti-scorch agent with thiazole or activated thiazole-type accelerators. (*Bull. No. 851*)

PEPTON® 22 Plasticizer

The application of this catalytic peptizer in natural and synthetic rubbers is reported. (*Bull. No. 816*)

PEPTON® 22 Plasticizer in Oil-Extended GR-S

Gives test results under conditions approximating those in the factory.

(*Bull. No. 816 Sup. No. 1*)

PEPTON® 65 and 65B Plasticizers

Describes these concentrated peptizers and their application to reduce milling time.

The above literature is available on request.

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CYANAMID

AMERICAN CYANAMID COMPANY

RUBBER CHEMICALS DEPARTMENT

Bound Brook, New Jersey

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General Tire's Chemical Division is constantly aware of the needs of the rubber industry, and provides these specially-formulated products to meet those needs. Write or call for further information and generous samples.

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GEN-TAC • Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.

KO-BLEND • Latex-compounded masterbatch, 85% insoluble sulfur colloiddally dispersed in SBR latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

KURE-BLEND MT • 50 SBR — 50 TMTD latex-compounded masterbatch. Gives faster, more even dispersion, allowing full advantage of TMTD accelerator. Assures uniform cure, at no premium cost.

RUBBER:

GENTRO • Top-quality cold SBR Polymers.

GENTRO-JET • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES:

GEN-FLO • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

ACRI-FLO • Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

PVC RESINS:

VYGEN • a complete family of top-quality, versatile resins formulated to meet specific needs.

THE GENERAL TIRE & RUBBER COMPANY
CHEMICAL DIVISION • AKRON, OHIO

Creating Progress Through Chemistry



HERE'S HOW WITCO-CONTINENTAL PROTECTSYOUR **CARBON BLACK** DOLLAR
THROUGH

*Quicker, More Dependable Shipments • Unmatched Care in Packaging
Outstanding Loading and Stacking Techniques
Faster, Cleaner Unloading and Handling*

**CARBON BLACKS . . . PRODUCED AND HANDLED
WITH CARE BY WITCO-CONTINENTAL**

Only Witco-Continental gives carbon blacks such kid-glove treatment in packaging and shipping. There's no compromise on quality and no compromise on service. Facilities are maintained in

every sales office city for ex-warehouse customers. For outstanding service and personalized attention on all your carbon black orders . . . be sure to specify WITCO-CONTINENTAL.



There's less chance of shipping delay with Witco-Continental carbon blacks. We print your purchase order number, code or pigment number, type of black and other information, on every bag. Result is easier inventory, checking and handling.

Improved packing and better palletizing are achieved through specially built bag-shaping machines. You choose the type of bag you want.

Valve bags mean better unit loading, cleaner warehousing, faster and easier handling. Witco-Continental's exclusive, patented valve-filling machines insure greater uniformity of outside bag dimensions.





When carbon blacks leave Witco-Continental plants, you can be sure they're in good condition. We photograph each shipment after loading as a check on correct and damage-free stacking. These photographs, with specially designed loading diagrams attached, are then sent to you as your check on shipping conditions.



Special car liners prevent interlocking of bags and protect them from each other and from the sides of cars or trailers. Convenient, disposable pallets facilitate handling, yet eliminate storage or return costs.



If you prefer shipment by hopper car, Witco-Continental traffic control system means that you can get same-day information on the whereabouts of your shipment from your local sales office. There are 113 carefully maintained hopper cars ready to serve you.



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THE STEREOREGULAR POLYMERIZATION OF ISOPRENE WITH LITHIUM AND ORGANO-LITHIUM COMPOUNDS *

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THE FIRESTONE TIRE AND RUBBER COMPANY, AKRON, OHIO

The use of the alkali metals and the alkali metal alkyls as polymerization catalysts, either alone or as components in more complex systems, is now familiar. However, it was completely unexpected when it was first found that lithium in systems free of oxygen-containing compounds such as ethers, which are the classical solvents for reactions involving organometallic compounds, catalyzed polymerization of isoprene to an essentially all *cis*-1,4 structure.

TABLE I
MICROSTRUCTURE OF POLYISOPRENE CATALYZED BY ALKALI METAL AND ALKALI METAL DERIVATIVES

Solvent	Catalysis	Infrared analysis				Total found, % ^b
		<i>cis</i> -1,4, % ^a	<i>trans</i> -1,4, %	1,2, %	3,4, %	
Pentane	Lithium	94.4	0.0	0.0	5.6	91.7
Pentane	Ethyllithium	94.2	0.0	0.0	5.8	92.0
Pentane	Butyllithium	92.6	0.0	0.0	7.4	88.9
Pentane	Sodium	0	43	6.0	51	—
Pentane	Ethylsodium	6.3	42	7.1	44.6	99.4
Pentane	Butylsodium	4.1	34.9	6.7	54.4	100.7
Pentane	Potassium	0	52	8	40	—
Pentane	Ethylpotassium	23.7	39.2	5.7	31.4	96.7
Pentane	Butylpotassium	19.6	40.8	6.2	33.5	94.2
Pentane	Rubidium ^c	5	47	8	39	—
Pentane	Cesium ^c	4	51	8	37	—
Pentane	Alfin (sodium) ^c	27	52	5	16	—
Pentane	Emulsion ^c	22	65	6	7	—
Pentane	Cationic	36.7	50.6	3.8	8.9	78.9
Ethyl ether	Ethyllithium	6.0	29.1	5.3	59.6	95.2
Ethyl ether	Ethylsodium	0.0	14.3	10.2	75.6	98.9
Ethyl ether	Lithium metal	4.0	26.7	5.7	63.5	100.4

^a % *cis* = 100[(*cis*-1,4)/Σ(*cis*-1,4 + *trans*-1,4 + 1,2 + 3,4)].

^b % total found = 100[Σ(*cis*-1,4 + *trans*-1,4 + 1,2 + 3,4)/total solids].

^c Data of Foster and Binder.¹⁰

From the data in Table I it is clear that, of all the metals in the first group of the periodic table, only lithium (or some of its compounds) is capable of producing a stereoregular polymer from isoprene. It is also of interest to note that the isotopes Li⁶ and Li⁷ which occur naturally in lithium have no effect on the polymer microstructure as shown by the data in Table II.

* Presented before the Division of Rubber Chemistry, 134th Meeting of the American Chemical Society, Chicago, Ill., September 10-12, 1958. Reprinted from the *Journal of Polymer Science*, Vol. 41, pages 381-397, 1959.

TABLE II
 POLYMERIZATION OF ISOPRENE WITH ISOTOPES OF LITHIUM

Li, atomic wt.	6.94	6.94	7	6	6
Monomer	100	100	100	100	100
Solvent	300	300	300	300	300
Li, % on monomer	0.04	0.05	0.15	0.05	0.0125
Initiation temp., °C	50	55	50	50	50
Propagation temp., °C	0	55	20	50	25
Conversion, %	100	100	100	100	100
Inherent viscosity	6.85	—	9.55	8.2	8.5
Gel, %	0.5	—	4.5	0	0.5
Infrared anal.					
<i>cis</i> -1,4, %	94.2	92.3	92.3	88.6	92.8
<i>trans</i> -1,4, %	0.0	0.0	1.2	3.1	0.7
1,2, %	0.0	0.0	0.0	0.0	0.0
3,4, %	5.8	7.7	6.5	8.3	6.5
Total found	91.4	94.7	85.6	89.0	91.1

While both the lithium catalyst system^{2,7,15,17,21} and the catalyst system^{1,8,13,14,16} involving aluminum alkyls and titanium tetrachloride lead to polyisoprenes having the essential characteristics of natural rubber, it is felt that there is little similarity in the mechanism of the polymerization reaction itself. It is extremely interesting that there should be *two* systems which are capable of bringing about the stereospecific addition of an isoprene unit to a growing polymer chain so that there is obtained the *cis*-1,4, head-to-tail structure. It is the purpose of this paper to suggest a mechanism for the lithium-catalyzed polymerization of isoprene.

POLYMERIZATION TECHNIQUES

The polymerization of isoprene with lithium and the organolithium compounds was conducted in the laboratory in pressure type polymerization bottles sealed with crown caps. Precautions were taken to avoid the presence of water and oxygen and other impurities which inhibit the polymerization or react with the lithium catalyst. The isoprene used in this work had a purity greater than 99 mole-%. Generally the polymerization was conducted in the presence of an inert hydrocarbon such as *n*-pentane.

When metallic lithium was used as a catalyst, a fine dispersion of the metal in petroleum jelly was prepared as described previously²¹. The organolithium compounds, such as butyllithium, were prepared by reacting the corresponding alkyl halide and the lithium dispersion in a hydrocarbon medium¹³. The activity of these compounds was routinely tested by the method of Gilman and Haubein¹¹.

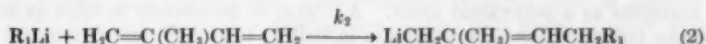
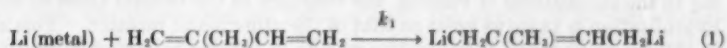
Infrared determination of microstructure was conducted as described previously by Binder⁸. Polymers were purified by dissolution in toluene, followed by precipitation with acetone prior to analysis. Inherent viscosity and gel content were determined by standard techniques⁹.

MECHANISM OF LITHIUM-CATALYZED POLYMERIZATION

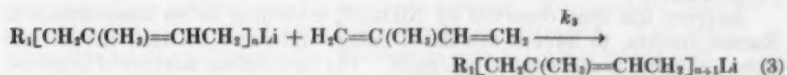
The mechanism of the *cis*-1,4 addition of isoprene in the lithium catalyst system has not been elucidated. The lithium system is unique in that a high degree of stereoregularity is obtained with as little as 5×10^{-5} mole/l of carbon-bound lithium (equivalent to 0.00025 g Li/100 g monomer in a 20% monomer-solvent solution) in the form of soluble alkylolithium which has been

carefully filtered to eliminate all unreacted lithium metal and lithium halide remaining from the synthesis of the catalyst. It appears that a second phase, such as a specific solid surface, is unnecessary and that this stereoregular polymerization proceeds through a homogeneous catalytic mechanism which depends on the electronic structure of the lithium atom, the molecular structure of isoprene, and their proper interaction for the formation of *cis*-1,4 polyisoprene. It should now be apparent that the mechanism of polymerization of isoprene with lithium to produce a *cis*-1,4 polymer is entirely different from that of the titanium tetrachloride/aluminum alkyl polymerization. In the latter instance, the molecular weight is highly dependent on the temperature of polymerization, and the microstructure is independent of the temperature and catalyst concentration¹.

The initiation of the polymerization reaction with lithium catalysts can be represented by the following equations:



Equation (1) represents the initiation reaction with lithium metal, and eq. (2) that with lithium alkyls. The rate constant k_1 is the rate of reaction of the finely divided dispersed lithium with the monomer to form a dilithium adduct. The rate constant k_2 is the rate of addition of a soluble alkyl lithium to the monomer. As is to be expected, our observations have indicated k_1 to be much smaller than k_2 . The propagation step may be represented as:



where k_3 is the rate constant. Any proposed mechanism must account for the stereoregularity of the propagation reaction represented by Equation (3). There are not sufficient data to support unambiguously (indeed, this is seldom possible) the reaction mechanism which is developed in the succeeding paragraphs. However, the available data do seem to indicate that the proposed mechanism (or activated complex) is not unrealistic in its approach.

Those properties of lithium that set it apart from the other members of the first group of the periodic table are the small basic radius of the lithium ion, 0.475 Å. compared to 0.875 Å. for sodium ion, and the tendency of lithium to

TABLE III
PHYSICAL CONSTANTS OF THE ALKALI METALS

	Pauling electro- negativity value	Ionic character of metal- carbon bond, %	Coulson's basic radii of ion, Å	Hybridization, % p character of	
				Metal	Molecule
Li	1.0	43	0.475	41	14
Na	0.9	47	0.875	27	7
K	0.8	52	1.185	26	6
Rb	0.8	52	1.320	26	5
Cs	0.7	57	1.445	28	6

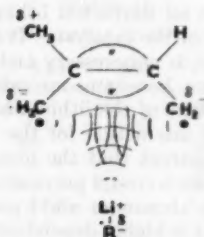


Fig. 1.—Schematic representation of the interaction of a growing polymer chain or catalyst molecule with isoprene in the *cis* configuration.

undergo hybridization of the *s* and *p* orbitals as shown in Table III. According to the calculations of Pauling, the tendency of the lithium atom to undergo hybridization is twice as great as that of the other alkali metals¹⁹. This ability of lithium to undergo hybridization results in lithium behaving in many of its reactions as a polyvalent atom. A degree of association as high as seven has been measured for *n*-butyllithium in boiling benzene²², and complexes such as $\text{Na}^+[\text{Ph}_2\text{Li}(\text{OEt}_2)]^-$ and $\text{Li}^+(\text{Ph}_2\text{Li})^-$ have also been prepared^{23,24}, demonstrating that lithium can attain a covalency of two or even three. A further property of lithium is the high degree of stereoretention exhibited in many of its reactions. It has been demonstrated that the lithium derivatives of the vinyl compounds retain their configuration about the double bond, both during the formation of the lithium compounds and after the replacement of the lithium⁶. Even the C—Li bond of saturated compounds has a surprising although small level of stereostability⁶.

Isoprene has been observed by Nikitin¹⁸, according to his observations of Raman spectra, to have a calculated energy difference between the *cis* and *trans* resonance isomers of 900 cal/mole. The equilibrium mixture of isoprene, according to Nikitin, contains 85% of the *cis* isomer at 50° C. The schematic diagram of Figure 1 adequately represents a probable distribution of electrons in this conjugated molecule, if the above statement concerning the configuration of isoprene in the liquid state is correct. In postulating a sequence of kinetic steps leading to the addition of a monomer unit in the *cis* configuration, a logical first step would be the formation of a complex between the carbon-bound lithium atom and *cis*-isoprene, as shown in Figure 1, where an attempt

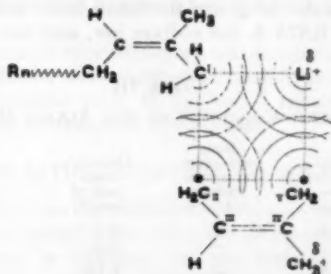


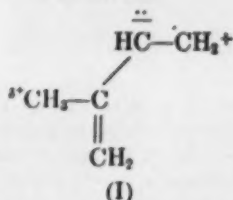
Fig. 2.—Schematic representation of the proposed activated complex leading to *cis*-1,4 addition in lithium-catalysed polymerization of isoprene.

has been made to illustrate the orbital overlap responsible for this coordination. Quantitative data on the stability of olefin-metal complexes show that olefinic hydrocarbons with *cis* configuration coordinate more strongly than those with *trans* configuration⁴. Further, no cases are known in which geometrically isomeric olefins are isomerized by coordination with and liberation from metal complexes. In this first step, advantage is taken of the tendency of lithium to react essentially with those resonating isoprene molecules which are in the *cis* configuration.

It is proposed that the *cis* coordination complex rearranges so that there is obtained an activated complex which geometrically can be represented as a six-membered ring, as shown in Figure 2. The addition of a monomer unit essentially involves the reaction of a *cis* isoprene molecule containing an unpaired electron on each of the two terminal carbon atoms with a polarized carbon-lithium bond. As carbon atom C_{II} approaches the carbon atom of the carbon-lithium bond, C_I , the C_I -Li bond is stretched. At the same time, as carbon atom C_V approaches the lithium atom the degree of orbital overlap becomes greater than for the stretched C_I -Li bond, and the strained C_I -Li bond now breaks, and the covalent carbon-carbon bond C_I - C_{II} is formed. The activated complex involved in this polymerization falls under Hughes' and Ingold's four-center type S_N1 reactions. The reaction appears to be analogous to the Diels-Alder reaction and the addition of nitroso compounds and of sulfur dioxide to conjugated dienes.

The mechanism of the *cis*-1,4-addition as postulated can be considered as the addition of a diradical to a polarized, but nonetheless covalent, carbon-lithium bond. The reaction cannot, therefore, be considered as a true example of anionic polymerization. This statement is substantiated by the essential slowness of the polymerization reaction as contrasted to the instantaneous reactions at low temperatures for true ionic systems. Furthermore, ionic polymerization reactions have very low energies of activation. The energy of activation for the polymerization of isoprene with lithium is rather high. The reaction proceeds very slowly below temperatures of -20°C , but extremely rapid reactions are obtained at 25°C .

A structure of the type postulated for the activated complex is adequate to explain the observed 93-95% essentially head-to-tail, *cis*-1,4-addition. The residual 5-7% 3,4-addition that is observed can be accounted for by the other resonance structures of isoprene, particularly Structure I:



which would lead to the direct transfer of the charged lithium atoms down the chain as polymerization progresses.

Sodium and other alkali metals form a carbon metal bond having ionic character almost equivalent to that of the carbon-lithium bond, but the degree of orbital hybridization is considerably less, and the basic ionic radius is con-

siderably greater. Therefore, the coordination complex and the cyclic activated complex proposed for lithium and isoprene would be unlikely with these metals. As is known, sodium and the remaining higher members of the alkali metal group catalyze the formation of polyisoprenes of a heterogeneous structure. The infrared analysis indicates substantially equal *trans*-1,4 and 3,4-structures together with the introduction of 6-8% of the 1,2-structure. There is little, if any, difference in the structures of polyisoprenes catalyzed by the alkali metals or alkali metal alkyls other than lithium.

The experimental evidence which to some degree appears to support the mechanism which has been proposed for the *cis*-1,4-addition of isoprene, when catalyzed by lithium, is presented in the following.

When a mixed dispersion of sodium and lithium is prepared in petroleum jelly, x-ray examination has shown that there is no alloying or compound

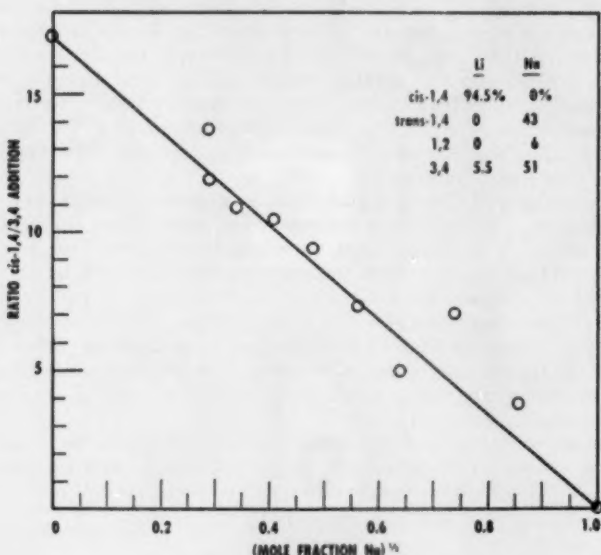
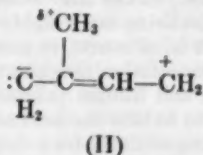


FIG. 3.—The effect of sodium on the microstructure of polyisoprene prepared by lithium-catalyzed polymerization.

formation, in agreement with the literature on mixtures of sodium and lithium²⁰. When these mixed dispersions were used to polymerize isoprene, it was found that the ratio of the *cis*-1,4- to the 3,4-addition could be represented as a linear dependence of the square root of the mole fraction of sodium present, as shown in Figure 3. The interesting point here is the linear dependence of the structure on the square root of the mole fraction of sodium. Apparently the free energy of activation ΔF^* required for a monomer unit to add to a chain end containing a sodium atom is considerably less than that required to react with a growing chain containing lithium. It seems probable, considering the almost total absence of *cis*-addition with sodium, that the activated complex leading to *trans*-1,4-addition involves the direct addition of a monomer unit to the anionic

end of a polymer chain. The electron distribution of isoprene adding to the growing polymer chain in this case would be represented by



leading to *trans*-1,4-addition. The 3,4-addition is accounted for by the resonance structure I. Polymerization with sodium and the other alkali metals is probably closely related to the classical anionic mechanism where propagation progresses through the direct transfer of charge. Ionic mechanisms, in general, are known to have activation energies lower than those for other types of reaction mechanisms. The Eyring free energy of activation for the propagation reaction may be split between the entropy term ΔS^\ddagger and the heat of activation ΔH^\ddagger . It seems likely that a portion of the difference between ΔF^\ddagger for sodium polymerization and ΔF^\ddagger for lithium polymerization could be caused by a lower ΔS^\ddagger for the propagation reaction with lithium, because of the loss in degrees of

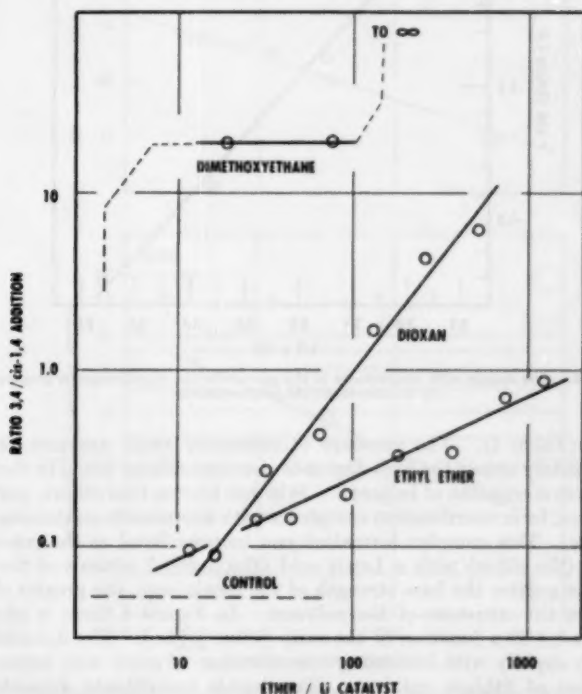


Fig. 4.—The effect of some ethers on the microstructure of polyisoprene prepared by lithium-catalysed polymerization.

freedom of the monomer in the cyclic activated complex proposed for the lithium propagation reaction. The remainder of the difference in ΔF^\ddagger between the two reactions lies, of course, in the ΔH^\ddagger term. Here it is to be expected that the sodium polymerization being more highly ionic in nature will have the smaller heat of activation. It is, of course, impossible from this experiment to make any statement as to the relative magnitude of the differences between ΔS^\ddagger and ΔH^\ddagger for the sodium and lithium polymerization. However, the observed relationship is such as to fit into the mechanism as described above.

Additional strong supporting evidence for a cyclic, activated complex in the case of lithium and isoprene is obtained from the effect of ethers on the microstructure of polyisoprene obtained in reactions catalyzed with the various alkali metals. When polymerization is conducted in ethyl ether, it is found that the stereospecific aspects of lithium are lost and the microstructure of polyisoprenes obtained in reactions catalyzed by all the alkali metals become more or less

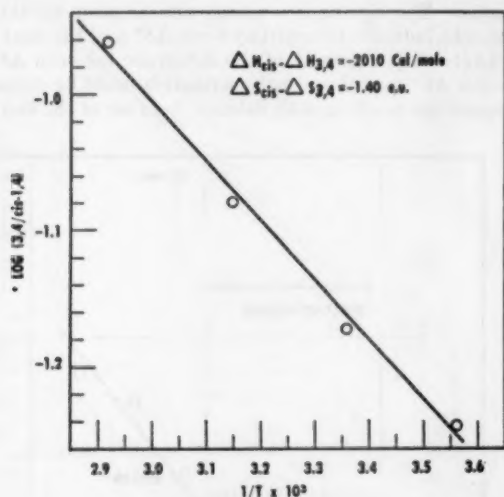


FIG. 5.—The change with temperature in the microstructure of polyisoprene prepared by lithium-catalyzed polymerization.

equivalent (Table I). The presence of extremely small amounts of methyl ethers completely upsets the high degree of stereospecificity found in the lithium-catalyzed polymerization of isoprene. It is well known that ethers, particularly methyl ethers, form coordination complexes with compounds containing carbon-metal bonds. This complex formation can be considered as the reaction of a Lewis base (the ether) with a Lewis acid (the unfilled orbitals of the lithium atom). The greater the base strength of the Lewis base, the greater should be the effect on the structure of the polymer. In Figure 4 there is plotted the ratio 3,4/cis-1,4 as a function of the ratio [ether]/[Li]. The 3,4-addition increases very rapidly with increasing concentration of ether with respect to the concentration of lithium catalyst. The double logarithmic dependence observed may be explained on the basis of an acid-base equilibrium between the ether and the lithium. For every addition of a monomer unit to a chain con-

taining a C—Li bond coordinated with an ether molecule, a 3,4- or a *trans*-1,4- rather than a *cis*-1,4-addition will occur. The greater effect of dioxane over ethyl ether is to be expected on the basis of the greater base strength of the dioxane. The effect of the methyl ether, dimethoxyethane, is much greater than expected. The tendency to promote 3,4-addition is so strong that at a molar ratio of ether to catalyst of 100 to 1 there is no longer any *cis*-1,4-addition product. Evidently, coordination of any Lewis base with the C—Li bond prevents the formation of the cyclic activated complex and favors an activated complex based on the charged resonance structure of isoprene (I and II).

The nature of the activated complex which has been postulated is such that there should be observed a pronounced temperature effect on the amount of *trans*-1,4- and 3,4-addition obtained. The amount of *trans*-1,4- and 3,4-addition increases with the temperature of polymerization. The effect of temperature on the 3,4-addition can be expressed by an Arrhenius-type equation as illustrated in Figure 5. From the eq. (4):

$$RT \ln (m/n) = \Delta H_m - \Delta H_n + T(\Delta S_m - \Delta S_n) \quad (4)$$

where m/n is the ratio of concentration of structure m to structure n , an ap-

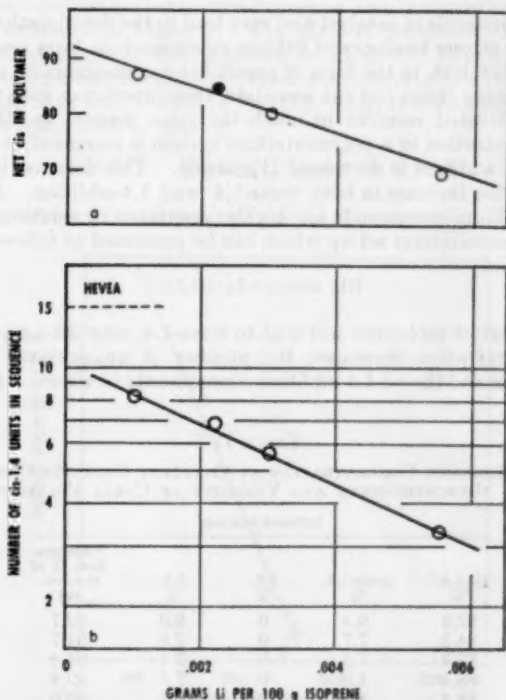


FIG. 6.—The effect of catalyst concentration on the microstructure of polyisoprene prepared by lithium-catalyzed polymerization: (a) the net *cis*-1,4 content of polymer prepared in the presence of (O) ethyllithium and (●) amyllithium is calculated as (% *cis*-1,4 × total found); (b) the number of *cis*-1,4 units, with the assumption of a uniform distribution is given by $(100 - \text{net } \textit{cis}\text{-1,4})$.

proximate difference between the heat and the entropy of activation can be calculated. It is found that:

$$\Delta H_{cis} - \Delta H_{3,4} = -2010 \text{ cal./mole} \quad (5)$$

$$\Delta S_{cis} - \Delta S_{3,4} = -1.4 \text{ e.u.} \quad (6)$$

According to these data, the overall activation energy leading to 3,4-addition is greater than that leading to *cis*-1,4-addition. Since it has been suggested that 3,4-addition is the result of an anionic mechanism, a lower activation energy for the 3,4-addition with respect to the *cis*-1,4-addition is to be expected. However, taking into consideration the cyclic association complex proposed for the *cis*-addition, this discrepancy can be rationalized. An increase in temperature should increase the dissociation of the carbon-lithium bond and thus make it more ionic and approach the C—Na bond in this respect. An increase in temperature would also be expected to increase the degree of dissociation of the *cis*-coordination complex with the monomer. Because of these two effects, the rate constant of the overall polymerization reaction is such as to make it appear as if the heat of activation for the 3,4-addition is larger than that for the *cis*-addition.

Excessive amounts of catalyst also may lead to the deterioration of structure because of the strong tendency of lithium compounds to form association complexes. The catalyst, in the form of organolithium compounds, and the active lithium-containing chain end can associate, thus interfering with the formation of a cyclic activated complex in much the same manner as ethers. As the catalyst concentration in a polymerization system is increased, it is found that the net *cis*-1,4 addition is decreased (Figure 6). This decrease in *cis*-1,4 is of course due to the increase in both *trans*-1,4- and 3,4-addition. Remembering that organolithium compounds are highly associated in solution, there is undoubtedly an equilibrium set up which can be presented as follows:



Associated catalyst molecules will lead to *trans*-1,4- and 3,4-addition. As the catalyst concentration decreases, the number of unassociated molecules of course increases and the *cis*-1,4-addition consequently increases. In this respect

TABLE IV
EFFECT OF MONOMER CONCENTRATION AT CONSTANT CATALYST CONCENTRATION
ON THE MICROSTRUCTURE AND VISCOSITY OF CORAL POLYISOPRENE*

Monomer, vol.-%	Infrared analysis				Unsaturation, % of theoretical	Inherent viscosity
	<i>cis</i> -1,4, %	<i>trans</i> -1,4, %	1,2, %	3,4, %		
2	82.6	9.4	0	8.0	92.7	—
5	84.5	7.7	0	7.8	91.7	4.79
10	85.4	7.5	0	7.1	94.4	7.04
15	88.4	4.0	0	7.5	89.4	8.48
20	88.4	4.1	0	7.5	89.0	8.31
25	87.1	4.7	0	8.3	87.3	7.88
30	84.7	6.4	0	8.9	88.4	7.54

* Catalyst concentration: 1.55×10^{-4} mole carbon-bound lithium (butyllithium)/l.

TABLE V
EFFECT OF CONVERSION ON INHERENT VISCOSITY OF POLYMER*

Conversion, %	Inherent viscosity
1.8	0.134
4.5	0.314
8.0	0.545
13.9	0.804
20.5	0.920
23.8	1.07
35.8	1.34
50.7	1.40

* Catalyst concentration: 0.0021 g carbon-bound lithium (as butyllithium) per hundred parts monomer; monomer concentration: 30% by volume; temperature of polymerization: 40° C.

it has been found that catalyst concentration affects the *cis*-1,4-addition more than temperature, at least over the temperature range 0–70° C.

The nature of chain transfer and chain termination reactions in the lithium catalyzed polymerization of isoprene has received little attention. The data presented below have some bearing on this subject.

It has been found that the inherent viscosity of the polymer increases linearly as the catalyst concentration decreases and is somewhat temperature independent as shown in Figure 7. The effect of monomer concentration at constant catalyst concentration is shown in Table IV. Further it has been found that the inherent viscosity increases with conversion as shown in Table V. These data have been plotted in Figure 8, where it is seen that the viscosity increases with conversion so that

$$1/\eta = a + (b/c) \quad (8)$$

where c is the degree of conversion and a and b are constants. The microstruc-

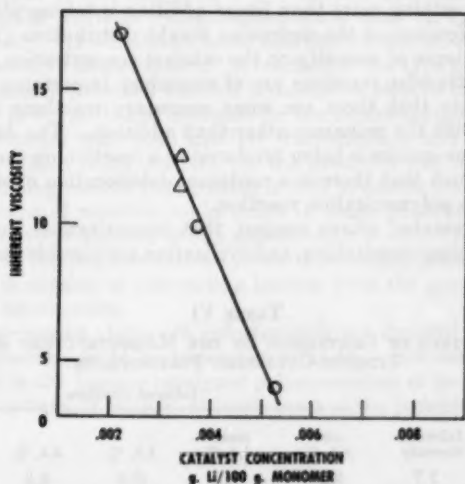


FIG. 7.—The effect of ethyllithium concentration on the viscosity of polyisoprene prepared by lithium-catalyzed polymerization at (O) 50° C and (Δ) 70° C.

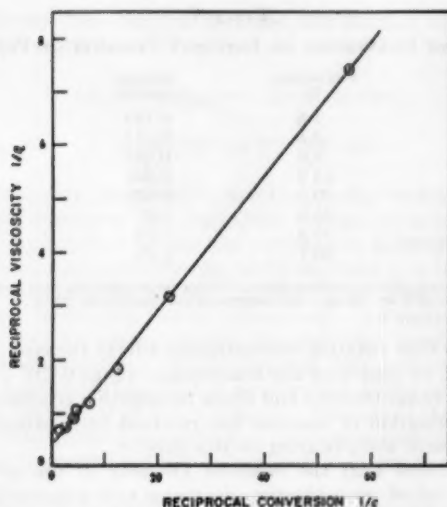


FIG. 8.—Increase in viscosity as a function of conversion for preparation of polyisoprene by lithium-catalyzed conversion at a monomer concentration of 30%, catalyst concentration of 0.002 g carbon-bound lithium (as butyllithium), and polymerization temperature of 40° C.

ture is also dependent on the conversion as shown in Table VI. Molecular weight distribution for a typical polymer as determined from fractionation is recorded in Table VII.

The changes in both microstructure and viscosity which have been observed during the course of a polymerization reaction are of sufficient magnitude to indicate that something more than linear addition is taking place. However, the extreme narrowness of the molecular weight distribution (Table VII) and the linear dependence of viscosity on the catalyst concentration (Figure 7) suggest that chain transfer reactions are of secondary importance. The data of Table IV indicate that there are some secondary reactions of the growing polymer chain with the monomer other than addition. The data of Table VI indicate that some species is being produced or a reaction on the polymer chain is taking place such that there is a continual deterioration of structure during the course of the polymerization reaction.

The data presented above suggest that isomerization, intra- and inter-molecular branching, crosslinking, and cyclization are possible reactions. These

TABLE VI
EFFECT OF CONVERSION ON THE MICROSTRUCTURE OF
LITHIUM-CATALYZED POLYISOPRENE

Conversion %	Inherent viscosity	Infrared structure				Unsaturation, % of theoretical
		cis- 1,4, %	trans- 1,4, %	1,2, %	3,4, %	
7.5	7.7	93.7	0.0	0.0	6.3	93.8
20	10.2	91.5	0.9	0.1	7.4	90.7
80	10.9	90.8	1.1	0.0	8.0	88.4

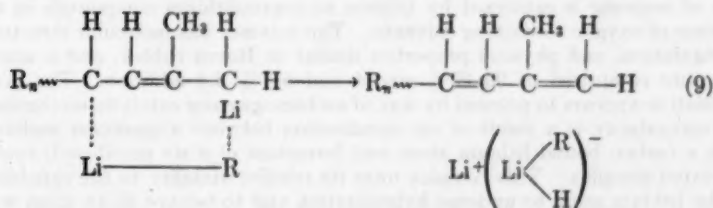
TABLE VII
MOLECULAR WEIGHT DISTRIBUTION OF A LITHIUM-CATALYZED
CORAL POLYISOPRENE*

Viscosity range	Polymer in each range, %
0-1	1.6
1-2	1.8
2-3	3.6
3-4	5.4
4-5	11.7
5-6	61.5
>6	13.0

* Catalyst concentration: 0.001 g carbon-bound lithium (as butyllithium) per hundred parts monomer; viscosity: of whole polymer: 5.5, or gel 0; of acetone extract 1.4%.

reactions may result in chain termination or chain transfer. Reactions of the following nature would lead to the observed results.

It is possible that a catalyst molecule or a polymer chain end containing lithium could react with a growing polymer chain:



The ionic complex of LiR and LiH, if it is capable of initiating further polymerization, should result in configurations other than *cis*-1,4-addition as described previously. It will also be noted that the reaction described in Equation (9) may also result in isomerization. A reaction of the type proposed is analogous to the generally proposed cationic termination step in the polymerization of olefins with Lewis acids and accounts for the experimentally observed deterioration in structure with both catalyst concentration and conversion. Another reaction which could account for the observed loss in unsaturation as polymerization progresses is the addition of LiR to double bonds in the polymer chain. This type of reaction could result in chain branching. Since, as we have also noted, there appears to be a deterioration in structure as the monomer concentration in the polymerization system is increased, it seems probable that the monomer is capable of abstracting lithium from the growing chain. This would lead to termination.

The data presented above are unfortunately not detailed enough to permit any rigorous conclusions to be drawn regarding the exact nature of the kinetic steps involved in the lithium catalyzed polymerization of isoprene. However, the data do illustrate, in outline, at least, some of the possible reactions.

CONCLUSION

It has been shown that lithium metal and organolithium compounds, when used as catalysts for the polymerization of isoprene, yield a polymer containing

93-95% *cis*-1,4 configuration and 5-7% 3,4-addition product. The catalytic mechanism in the case of lithium and its compounds, irrespective of their solubility, appears to be homogeneous.

It is suggested that the formation of a stereoregular polymer from isoprene and lithium is the result of the C—Li bond forming a coordination complex with the monomer in the *cis* configuration followed by rearrangement of this coordination complex to form a six-membered, cyclic, activated complex. The stability of the complex is a result of the ability of the lithium atom to undergo partial hybridization and thus assume a valency greater than one. Lewis bases, such as ethers, change the stereospecific aspects of the lithium-catalyzed polymerization of isoprene by the formation of a stable complex between the base and the carbon-bound lithium. This complex between the ether and the C—Li bond increases the ionic character of the C—Li bond to the extent that it becomes equivalent to that of the C—Na bond.

SYNOPSIS

All of the alkali metals catalyze the polymerization of dienes such as butadiene and isoprene. A stereoregular polymer is obtained when the polymerization of isoprene is catalyzed by lithium or organolithium compounds in the absence of oxygen containing solvents. The polymer has molecular structure, configuration, and physical properties similar to Hevea rubber, and a microstructure comprised of 93-95% *cis*-1,4 and 5-7% 3,4 addition. The polymerization appears to proceed by way of an homogeneous catalytic mechanism. Stereoregularity is a result of *cis* coordination between a monomer molecule with a carbon bound lithium atom and formation of a six membered, cyclic, activated complex. This complex owes its relative stability to the capability of the lithium atom to undergo hybridization and to behave as an atom with considerable divalent character. The observed effects of temperature, catalyst concentration, type of solvent, and effect of Lewis bases such as ethers on the microstructure of these isoprene polymers are consistent with the catalytic reaction mechanism advanced.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Adams, H. E., Stearns, R. S., Smith, W. A. and Binder, J. L., *Ind. Eng. Chem.*, **50**, 1508 (1958); *RUBBER CHEM. & TECHNOL.* **31**, 838 (1958).
- ² Alliger, Glen, Willis, James M., Smith, Ward A. and Allen, John J., *Rubber World* **134**, 549 (1956).
- ³ Binder, J. L. and Ransaw, H. C., *Anal. Chem.*, **29**, 593 (1957).
- ⁴ Chatt, J., "Cationic Polymerization", p. 45, W. Hoffer and Sons Ltd., Cambridge, 1953.
- ⁵ Cram, D. J., Allinger, J. and Langemann, A., *Chem. & Ind.*, (London), 1955, 919.
- ⁶ Austin, D. Y., Johnson, H. W., Jr. and Steiner, G. G., *J. Am. Chem. Soc.*, **77**, 4566 (1955).
- ⁷ Diem, Hugh E., Tucker, Harold and Gibbs, C. F., paper presented before Division of Rubber Chemistry, New York, Sept. 13, 1957.
- ⁸ Dinamore, Ray P., *Chem. Eng. News* **33**, 4518 (1955).
- ⁹ Ewart, R. H., "Advances in Colloid Science", Vol. II, p. 197, Interscience Publishers, Inc., New York, 1946.

- ¹⁵ Foster, F. C. and Binder, J. L., *Handling and Uses of Alkali Metals*, Am. Chem. Soc. Monograph No. 19, 1957.
- ¹⁶ Gilman, Henry and Haubein, A. H., *J. Am. Chem. Soc.* **66**, 1515 (1944).
- ¹⁷ Gilman, Henry, Langham, W. and Moore, F. W., *J. Am. Chem. Soc.* **62**, 2333 (1940).
- ¹⁸ Gibbs, C. F. et al. (to Goodrich-Gulf), Belgian 543,292 (June 2, 1956).
- ¹⁹ Horne, S. E., Jr., Kiehl, J. P., Shipman, J. J., Folt, V. L., Gibbs, C. F., Wilson, E. A., Newton, E. B. and Reinhart, M. A., *Ind. Eng. Chem.* **48**, 784 (1956); *RUBBER CHEM. & TECHNOL.* **29**, 687 (1956).
- ²⁰ Haieh, H., Kelley, Donald J. and Tobolsky, Arthur V., *J. Polymer Sci.* **26**, 240 (1957).
- ²¹ Kenney, R. P., *Rubber & Plastics Age* **38**, 1042 (1957).
- ²² Morita, Hirokazu and Tobolsky, Arthur V., *J. Am. Chem. Soc.* **79**, 5853 (1957).
- ²³ Nikitin, V. N. and Yakovleva, T. V., *Zhur. Fis. Khim.* **28**, 696 (1954); *Chem. Abstr.* **49**, 5966 (1955).
- ²⁴ Pauling, L., *Proc. Roy. Soc. (London)* **A196**, 343 (1949).
- ²⁵ Sittig, M., "Sodium, Its Manufacture, Properties and Uses", p. 73, Reinhold, New York, 1956.
- ²⁶ Stavely, F. W. et al., *Ind. Eng. Chem.* **48**, 778 (1956); *RUBBER CHEM. & TECHNOL.* **29**, 673 (1956).
- ²⁷ Wittig, G., Ludwig, R. and Poster, R., *Chem. Ber.* **88**, 294 (1955).
- ²⁸ Wittig, G., Meyer, F. J., and Lange, G., *Ann. Chem.* **571**, 167 (1951).
- ²⁹ Wittig, G., *Angew. Chem.* **70**, 65 (1958).

THE CATALYTIC POLYMERIZATION OF ISOPRENE WITH BUTYLLITHIUM *

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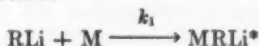
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The polymerization of isoprene through the action of free radicals and different catalysts has been studied in sufficient detail¹⁻⁴; as far as the polymerization of isoprene with butyllithium is concerned, apart from a few reports^{5,6}, no other pertinent publications have appeared.

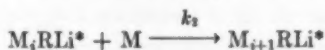
Isoprene in solution in saturated hydrocarbons, at moderate temperatures and in the presence of butyllithium as catalyst, polymerizes with remarkable rapidity. After mixing the solutions of monomer and catalyst, a slight induction period is observed, whereupon the polymerization reaction proceeds at a rate which is between first and second order with respect to the monomer. Since the reaction for polymerizing isoprene with butyllithium is of a homogeneous nature, a direct proportionality was anticipated between the rate of reaction and the catalyst concentration. It was discovered, however, that if direct proportionality does exist, it is found only within the range of very small concentrations of butyllithium; at higher concentrations of catalyst the reaction rate remains practically constant. The presence of such a relation was verified experimentally for four polymerization temperatures in two independent series of experiments.

The existence of an induction period and of a complex dependence of the reaction rate on the catalyst and monomer concentrations provided a basis for regarding the polymerization of isoprene with butyllithium as a case of chain catalysis. From the observations of such relationships in the present work, a satisfactory explanation was found for the supposition that the polymerization reaction is a composite of the following elementary reactions:

a) A chain initiation reaction, consisting of the reaction of the lithium organic compound with the monomer, leading to the formation of active centers in the polymerization reaction:



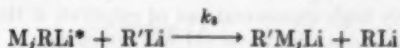
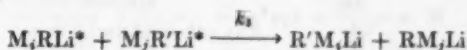
b) A chain growth reaction consisting of a succession of additions of monomer molecules to the active polymeric molecules, in such a way that with each and every elementary act up to the termination of the growing polymeric chain, the structure of the active centers is preserved:



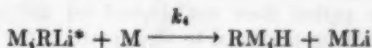
c) A chain termination reaction caused by the reaction of the active molecules with their analogs, or with the molecules of the catalyst, leading to forma-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by G. Leuca, from *Vysokomolekulyarnye Soedineniya* Vol. I, No. 1, pages 46-57 (1959).

tion of stable organometallic compounds, capable of serving as a basis for new reactive chains:



d) Chain transfer reactions, consisting of the reaction of active molecules with the monomer, to produce stable (inactive) polymeric molecules and organometallic compounds, capable of furnishing a basis for new reactive chains:



It appears that this last elementary reaction can be considered equally as well as a reaction which deactivates the growing chain, or a termination reaction.

We introduced the following designations:

m —monomer concentration;

$n = [R Li] + \sum_{j=1}^{\infty} RM_jLi$ —concentration of metallorganic compounds and

$n^* = \sum_{j=1}^{\infty} M_jRLi^*$ —the concentration of active molecules.

With catalytic polymerizations, neglecting the decomposition of the catalyst at the expense of secondary constituents, the overall concentration of metallorganic compounds and active molecules during the course of the whole process is equal to the initial concentration of the catalyst, i.e., $n_0 = n + n^*$. Under conditions of a quasi-stationary state of the system, when $k_1 \cdot n \cdot m = k_3 n^* n_0$

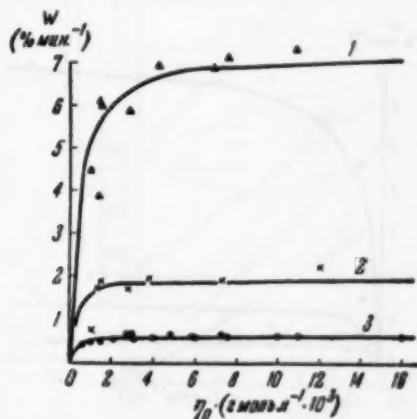


FIG. 1.—Dependence of the rate of polymerization of isoprene, in the quasi-stationary period, on the concentration of butyllithium (first series of experiments). Curve 1: 50°, calculated for $k_2 = 220$, $k_2/k_1k_3 = 17$, $m_0 = 1.90$ g-mol/l; Curve 2: 40°, calculated for $k_2 = 90$, $k_2/k_1k_3 = 90$, $m_0 = 1.93$ g-mol/l; Curve 3: 30°, calculated for $k_2 = 30$, $k_2/k_1k_3 = 290$, $m_0 = 1.94$ g-mol/l. Abscissa: η_0 (g-mol/l $\cdot 10^{-2}$).

+ $k_4 n^* m$, the rate of the polymerization reaction is described by the equation:

$$W = - \frac{dm}{d\tau} = k_2 n^* m = \frac{k_1 k_2 n_0 m^2}{(k_1 + k_4)m + k_3 n_0} \quad (1)$$

At comparatively high concentrations of catalyst, if there is sufficient disparity: $k_3 n_0 \gg (k_1 + k_4)m$, Equation (1) will appear as:

$$W = \frac{k_1 \cdot k_2}{k_3} m^2$$

Consequently, under these conditions the polymerization reaction rate in the quasi-stationary period does not depend on the concentration of the catalyst and is directly proportional to the square of the concentration of the monomer. Indeed, when there is a wide range in the concentration of butyllithium (from about 0.001 – 0.002 to 0.016 g-mole/l), the polymerization rate varies only infinitesimally (see Figures 1 and 2). In a plot of the rate of polymerization against the square of the average concentration of the monomer, the experimental points lie on straight lines which go through the origin (see Figure 3, Curves 2 and 3).

With low catalyst concentrations, when $k_3 \cdot n_0 \ll (k_1 + k_4)m$, Equation (1) will appear as:

$$W = \frac{k_1 \cdot k_2}{(k_1 + k_4)} n_0 \cdot m. \quad (3)$$

In the case of isoprene polymerization, the inequality: $k_3 n_0 \ll (k_1 + k_4)m$ will obtain for low concentrations of butyllithium; at concentrations of this order of magnitude the contaminants will poison the catalyst, and such impurities are inevitably present in the monomer and the solvent. That is why we did not succeed in obtaining reproducible results in our isoprene polymerizations for very low butyllithium concentrations, and the correctness of Equation (3) was confirmed experimentally in the following way.

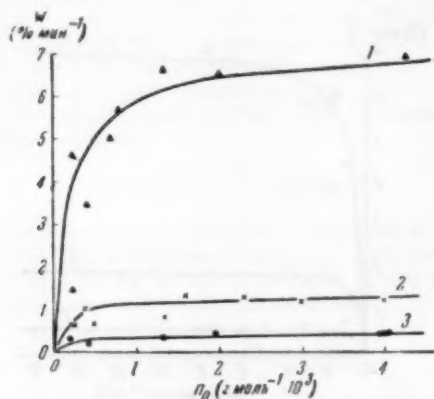


Fig. 2.—Dependence of the rate of isoprene polymerization, in the quasi-stationary period, on the butyllithium concentration (second series of experiments). Curve 1: 55°C, calculated for $k_2 = 420$, $k_2/k_1k_3 = 17$, $m_0 = 1.90$ g-mol/l; Curve 2: 40°C, calculated for $k_2 = 90$, $k_2/k_1k_3 = 90$, $m_0 = 1.93$ g-mol/l; Curve 3: 30°C, calculated for $k_2 = 30$, $k_2/k_1k_3 = 260$, $m_0 = 1.94$ g-mol/l. Abscissa: n_0 (g-mol/l · 10³); ordinate: (W min.⁻¹).

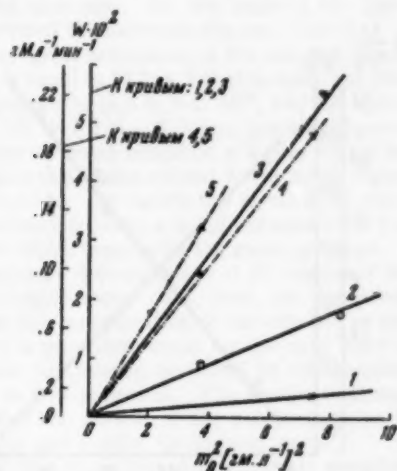


FIG. 3.—Set of straight lines used to calculate the value of the ratio for the constants: k_2/k_1 . Straight line 1 = 20°; 2 = 30°; 3 = 40°; 4 = 50°; and 5 = 55°. Abscissa: m_0^2 (g·mol⁻¹)²; ordinate: $W \cdot 10^2$ (g·mol⁻¹ min.⁻¹). Left scale (0–2.2): refers to Curves 4 and 5; right scale (0–5): refers to Curves 1 and 3.

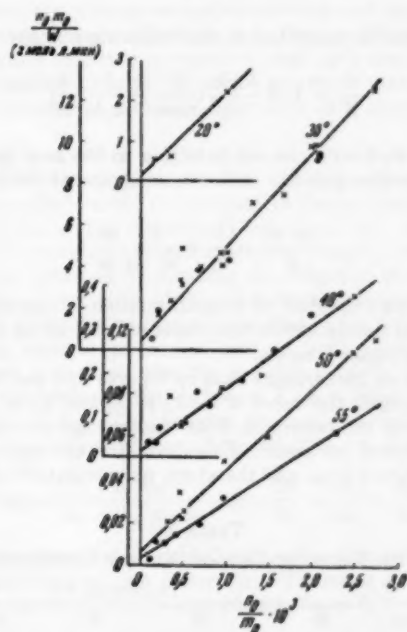


FIG. 4.—Dependence of $n_0 m_0 / W$ on n_0 / m_0 . Experimental points: x—first series, o—second series of experiments.

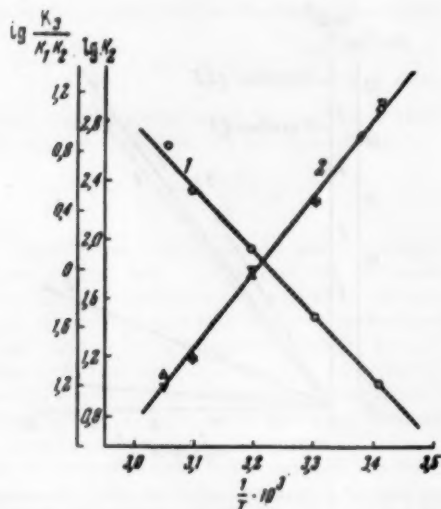


FIG. 5.—Dependence of $\log k_2$ (straight line 1) and $\log k_3/k_1k_2$ (straight line 2) on the reciprocal of the absolute temperature.

Equation (1) can be presented in the following manner:

$$\frac{1}{W} = 1 + \frac{k_4/k_1}{k_2} \cdot \frac{1}{n_0 m} + \frac{k_3}{k_1 k_2} \cdot \frac{1}{m^2} \quad (4)$$

Since the ratio $k_4/k_1 \ll 1$, its contribution to the sum in the first term of Equation (4) can be disregarded. After rearrangement the equation appears as follows:

$$\frac{n_0 \cdot m}{W} = \frac{1}{k_2} + \frac{k_3}{k_1 \cdot k_2} \cdot \frac{n_0}{m} \quad (5)$$

Actually, with the exception of a small number of experiments (see Figure 4), the experimental points within the limits of error lie on straight lines when $n_0 \cdot m_0/W$ is plotted against n_0/m_0 .

From the slopes of the straight lines in Figures 3, 4 and 5, we found that it was possible to calculate the value of k_2 , $k_3/k_1 \cdot k_2$ and k_4/k_1 (see Table I).

For calculation of the constants from the average reaction rate during the quasi-stationary period we assumed the rate for the period of the isoprene conversion to be 0.1 to 0.3 m_0 , and therefore, we calculated 0.8 m_0 as the average

TABLE I
THE VALUE OF CERTAIN KINETIC CONSTANTS

Figure	Temperature, ° C					
	20	30	40	50	55	
$k_2/k_1 \cdot k_2$	3	1220	296	93	25	19
$k_3/k_1 \cdot k_2$	4	1300	279	92	24	16
k_2	4	10.4	30.5	80.5	221	418
k_3/k_1	5	120	96	78	65	59

concentration of the monomer. On the basis of the derived values for the constants we constructed the curves in Figures 1 and 2.

The apparent energy of activation, in the reaction involving the growth of the polymer chain, is equal to 19.7 ± 2 kcal/g-mole, the pre-exponential factor in the Arrhenius equation is $(5.0 \pm 0.4) \cdot 10^{15}$, and the difference in the energy of activation $E_3 - (E_1 + E_2)$ is -23.5 kcal/g-mole (Figure 5). Consequently the activation energy for chain initiation is higher by 3.8 kcal/g-mole than for chain termination and this is also related to the much higher value of the constant k_3 as compared to k_1 . As regards the values of the pre-exponential factor, that for the chain initiation reaction is, for example, only five times larger than that for the reaction which terminates the growing chains.

Generally the separate determination of the values of the constants k_1 and k_3 is obtained, *via* experimental data, from the dependence of the average molecular weight on the concentration of the catalyst or the monomer.

In our case such a procedure could not be used since the high molecular weight metallorganic compounds produced in the termination reaction appeared to give rise to new polymers. The termination reaction leads only to the circumstance that the growth of the polymer chains becomes a reaction which runs irregularly and jerkily, by fits and starts.

After activation, the molecules of the original metallorganic compounds, due to the reaction with the first molecules of the monomer, quickly add a certain number of monomer molecules and deactivation takes place with formation of new metallorganic compounds. After the lapse of a certain length of time, the molecules of the thusly formed, comparatively high molecular weight metallorganic compounds are activated anew and there is rapid addition of monomer molecules, plus deactivation, *etc.* Such an irregular process for the growth of the polymer molecule is repeated until such time as there is no loss in weight of the monomer or until the active polymeric molecule does not react further with the monomeric molecule by means of a chain transfer reaction mechanism.

Thus the average molecular weight of the resultant polymer, as well as the molecular weight distribution, probably does not differ from the corresponding values for polymers which would be obtained in the polymerization of isoprene in the absence of one of the elementary reactions, *viz.*, interruption of the growing chain. The number average molecular weight, obviously, should be equal to the fraction obtained by dividing the weight of the resultant polymer by the total number of molecules of the catalyst in question, while the number of neutral polymer molecules might be calculated in the following manner: the rate for obtaining neutral molecules (p) evidently can be derived from the equation: $dp/d\tau = k_1 n^* \cdot m$ and the reaction rate for the polymerization: $-dm/d\tau = k_2 n^* \cdot m$; consequently, $dp/dm = k_1/k_2$. After integrating, we obtained $p = k_1(m_0 - m)/k_2$. The weight average molecular weight of the polymer obtained at total completion of the reaction ($m = 0$) will be:

$$M_r = \frac{68 m_0}{n_0 + k_1 \cdot m_0 / k_2} \quad \text{or} \quad \frac{68}{M_r} = \frac{n_0}{m_0} + \frac{k_1}{k_2}$$

In reality the experimental points fall approximately on straight lines when $1/M_r$ is plotted against n_0/m_0 (see Figure 6). The slope of the straight lines in Figure 6 correspond to the condition that when $k_1/k_2 = 0$, the following equation holds true:

$$\frac{1}{M_r} = \frac{1}{68} \frac{n_0}{m_0}$$

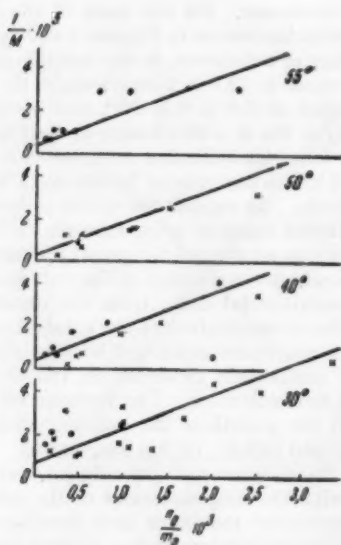


FIG. 6.—Dependence of the reciprocal of the molecular weight, on the ratio of the initial concentration of butyl lithium (m_2) and isoprene (m_1), for four temperatures; experimental points: X—first series, and ●—second series of experiments.

The large scattering of the points was due to two basic reasons: the error in dosage of the catalyst and the occurrence of a variable degradation of the samples of polyisoprene in the course of the viscosity determinations. When isoprene is polymerized at 30°, the constant for the reaction rate of chain transfer, and therefore, the reaction rate as well, is, for example, 2000 times less than the reaction rate for chain growth. With increase in polymerization temperature the relative importance of the chain transfer reaction is rather considerably reduced (at 50° the ratio of $k_2/k_4 \cong 5000$) inasmuch as the activation energy of the chain transfer reaction is at the expense of the monomer, for example, it is 9 kcal/g-mole less than the activation energy for the chain growth reaction. Such low values for the constant k_4 , in comparison with the value of k_2 , are dependent on the unusually low (for example of the order of 10) value for the pre-exponential factor.

Consequently, for two competing reactions:

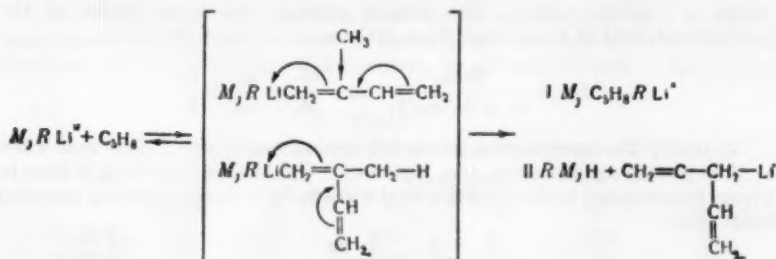


TABLE II
VALUES FOR VISCOSITY AVERAGE AND OSMOTIC AVERAGE
MOLECULAR WEIGHTS OF POLYMERS

No. of experiment (first series)	14	13	10	4	1
\bar{M} —viscometric ($\times 10^{-3}$)	955	64	345	121	69
\bar{M} —osmotic ($\times 10^{-3}$)	630	50	322	134	77
Polymerization temperature	40	40	50	50	50

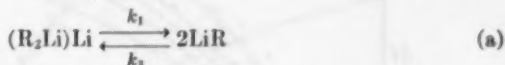
Although the second displays a lower activation energy, it runs slower by several orders of magnitude because of steric hindrance and entropy factors.

The first reaction was exothermic, —15.5 kcal/g-mole, while the second probably proceeded without appreciable liberation of heat.

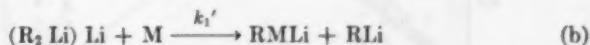
Since the chain transfer reaction with the monomer does not play an important role and if the value k_1 was different by an order of 2 or 3 from the value k_2 it follows that the molecular weight distribution of the isoprene polymer must be very narrow, with a distribution curve that approximates the Gaussian curve. In this case the number average and weight average molecular weights of the polymer coincide. We measured, in some experiments, besides the average viscometric molecular weight, the average osmotic weight (see Table II). The correspondence within the limits of error (except for Experiment 14) of the two average molecular weights gives a basis for the view that the polyisoprene appears to be very homogeneous in regard to molecular weight distribution.

The results of the measurement of the 1, 2 and 3, 4 content of isoprene units in some of the polymer samples showed that the microstructure does not depend on the polymerization temperature, nor on the initial concentration of the catalyst and monomer: the overall content of 1,2 and 3,4 units lies within a range of 5–7%.

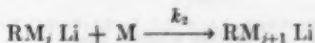
In recent times the opinion has been expressed that the polymerization of diolefins having conjugated double bonds, with metallorganic compounds of the alkali metals, involves a reaction having a stepwise mechanism^{7,8}. The fact discovered by us, that there is a dependence of the reaction rate on the initial concentration of butyllithium appears, at first glance, to be explainable by the presence of a dimerization reaction involving the metallorganic compounds in solution^{9,10}. Based on the representation of a stepwise reaction mechanism, the polymerization process can be interpreted in the following manner: with polymerization there is an increase in the monomeric molecules of the metallorganic compounds, obtained as a result of the spontaneous dissociation of the dimers:



or as a result of the reaction with isoprene:



The growth of the polymer chain consists of a stepwise addition of the molecules of isoprene, with the formation, at each step, of new lithium organic compounds:



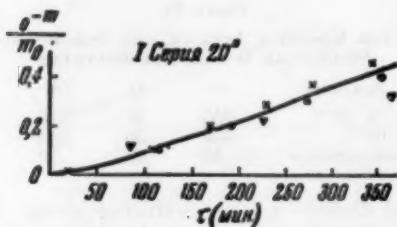
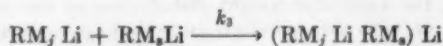


FIG. 7.—First series of experiments, kinetic curves at a reaction temperature of 20°. Initial concentration of butyl lithium (g-mol/l \cdot 10 3): ∇ = 0.6; \times = 1.0; \bullet = 3.0. Abscissa: time in min.

Deactivation of the growing chain consists of a dimerization reaction:



Evidently the concentration of lithium organic compound, as a monomer in solution in the presence of reaction (a) can be determined *via* the equation:

$$K = \frac{[LiR]^2}{[(R_2Li)Li]}$$

or, in the presence of reaction (b) by means of the equation:

$$k_1' [(R_2Li)Li][M] = k_3 [LiR]^2,$$

since, at all times, $n_0 = n + 2 [(R_2Li)Li]$, when $n = [LiR]$. Therefore the polymerization reaction rate in the first case will be:

$$W = k_2 \cdot n \cdot m \times \frac{1}{2} k_3 K \cdot m \{ (1 + 8n_0/K)^{1/2} - 1 \}$$

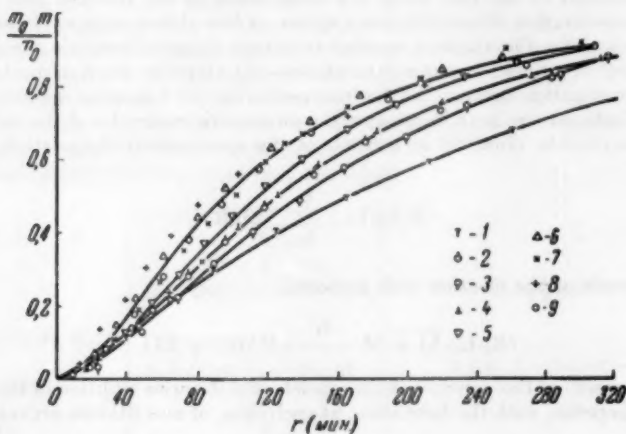


FIG. 8.—30°: 1—0.6; 2—1.0; 3—1.5; 4—1.5; 5—2.1; 6—2.7; 7—2.9; 8—3.0; 9—4.8. Abscissa = time in min.

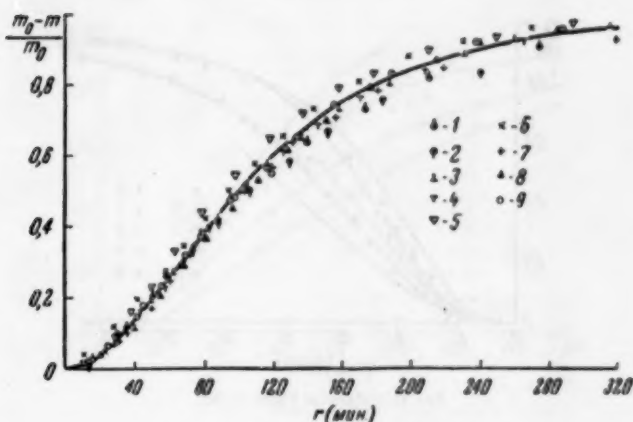


FIG. 9.—30°: abscissa = time in min.

and in the second

$$W = \frac{k_1 \cdot k_2 m^2}{4k_3} \left\{ \left(1 + \frac{8k_3 \cdot n_0}{k_1' \cdot m} \right)^{\frac{1}{2}} - 1 \right\}$$

When the value of n_0 is high, with $(8n_0/K)^{\frac{1}{2}} \gg 1$ or $(8k_3 \cdot n_0/k_1' m)^{\frac{1}{2}} \gg 1$, the equations are:

$$W = 0.707 k_2 \cdot K^{\frac{1}{2}} \cdot n_0^{\frac{1}{2}} m$$

$$W = 0.707 k_2 \left(\frac{k_1'}{k_3} \cdot n_0 \right)^{\frac{1}{2}} m^{\frac{1}{2}}$$

Consequently, at high concentrations of the catalyst, the rate of polymerization must be proportional to the square root of the catalyst concentration and to the first or one and a half power of the monomer concentration, respectively.

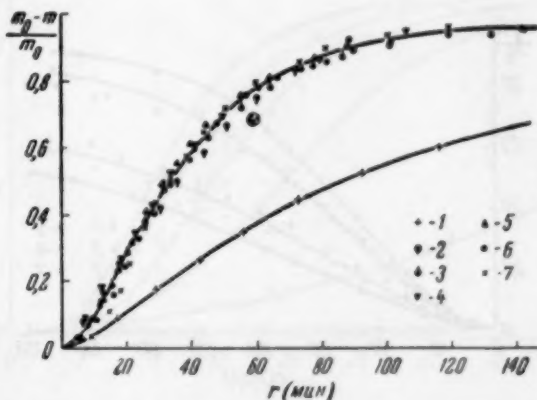


FIG. 10.—40°.

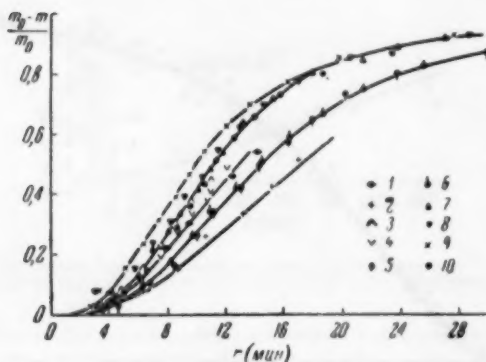
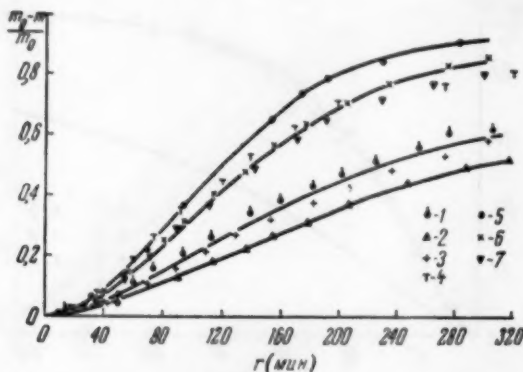


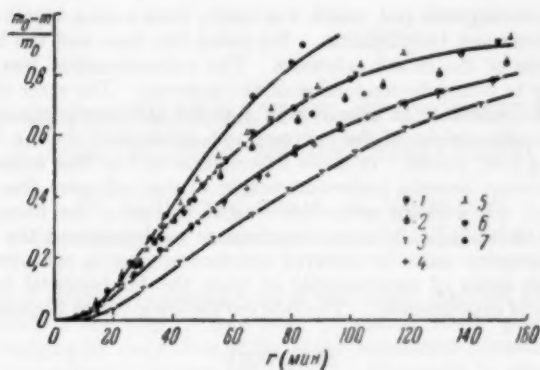
FIG. 11.—(Same as Figure 7) 50°.

Thus, our experimental data, for example in the polymerization of isoprene with butyllithium, appears to be additional proof that polymerization reactions of diolefins with metallorganic compounds and, apparently, with the metal alkyls, are connected with reactions exhibiting a complicated catalytic mechanism, and not with stepwise polymerization reactions representing simple metallorganic syntheses.

EXPERIMENTAL

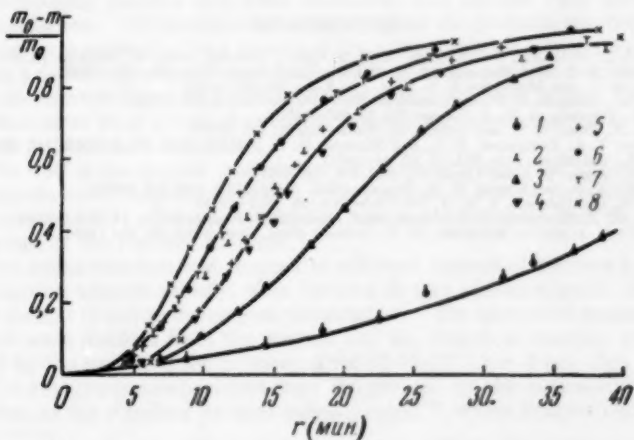
The dilatometric method was used to study the kinetics of isoprene polymerization. The polymerization vessel had two compartments (capacity 40–50 ml) with connecting tubes graduated at 0.1–0.2 ml and separated by a thin glass partition at the bottom of one of the compartments. The unit was heated at 200–250° *in vacuo* (residual pressure 2–5 mm) for a period of 2–4 hours. One of the compartments of the vessel was filled according to a recent condensation method, for example, with 20 ml of carefully purified solvent (in the first series of experiments with benzine gas and in the second series with

FIG. 12.—Second series of experiments, kinetic curves at a reaction temperature of 30°. Initial concentration of butyl lithium (g-mol/l⁻¹ · 10²).

FIG. 13.— -40° .

n-hexane) and 10 ml of isoprene, which was fed in from the device for filling the vessel. The final purification of the solvent and of the isoprene was carried out in successive double distillations with butyllithium. The technical isoprene used, according to analysis by means of maleic anhydride, was 99.8–99.9% isoprene. Into the other compartment of the vessel, likewise after careful heating *in vacuo*, we introduced the necessary quantity of the solution of butyllithium in benzine gas (first series) or in *n*-hexane (second series) and resealed it also. The butyllithium solution we obtained directly through the reaction of metallic lithium with chlorinated butyl in a suitable solvent. The concentration of butyllithium in the solution was determined according to the method of double titration¹¹.

After this, while maintaining the contents of the vessel at a constant, controlled temperature we broke the partition by shaking the vessel, or with the

FIG. 14.— -55° .

aid of an electromagnetic rod, which was inside, thus mixing together the solutions of isoprene and butyllithium. We noted the time and the level of the initial contents of the mixed solutions. The polymerization was conducted practically up to complete conversion of the isoprene. The error of the measurement of the reduction in volume was $\pm 2-4\%$ (relatively speaking). The average molecular weight of the polymer was determined by the viscometric method, using four points. In some experiments of the first series we determined the average osmotic molecular weight of the polymers (see Table II). We calculated the average molecular weight by using the formula: $\log M = 5.00 + 1.162 \log [\eta]$. In other experiments we determined the sum of the 1,2 and 3,4 isoprene units by infrared spectroscopy using the overtone¹² frequencies (first series of experiments) or from the fundamental frequencies¹³ (second series of experiments). The rate curves are given in Figures 7-14.

SUMMARY

1. The kinetics for the polymerization of isoprene with butyllithium in a solution of saturated hydrocarbons were determined.

2. The reaction has the mechanism of a chain catalytic reaction, in which active centers appear that are involved complexes formed from metallorganic compounds and monomer-polymer molecules.

3. Deactivation of growing chains takes place as a result of the reaction of active centers with each other or with metallorganic compounds. With this there are formed new metallorganic compounds of high molecular weight capable of becoming new polymerization centers.

4. The polymer possesses a narrow range of molecular fractions, closely approximating the Gaussian distribution, but the value of the average molecular weight of the polymer after completion of polymerization is inversely proportional to the catalyst concentration.

5. The polymerization temperature, and also the concentrations of the monomer and catalyst, do not affect the microstructure of the polymer (content of 1,2 and 3,4 isoprene units).

REFERENCES

- ¹ Bolland, L. J., *Proc. Roy. Soc. (London)* **A178**, 24 (1941); *RUBBER CHEM. & TECHNOLOGY* **14**, 811 (1941).
- ² Gantmacher, A. R., and Medvedev, S. S., *Doklady Akad. Nauk SSSR* **100**, 275 (1955).
- ³ Sheinker, A. A., and Medvedev, S. S., *Zhur. Fiz. Khim.* **29**, 250 (1955).
- ⁴ Morton, M., Salatiello, P. P., and Landfield, H., *J. Polymer Sci.* **8**, 279 (1952).
- ⁵ Haich, H., Tobolsky, A. V., *J. Polymer Sci.* **25**, 245 (1957).
- ⁶ Gibbs, C. F., Diem, H. E., and Tucker, H., *Rubber Age* **81**, 636 (1957).
- ⁷ Kropachev, V. A., Dolgoplosk, B. A., and Nikolaev, H. I., *Doklady Akad. Nauk SSSR* **115**, 737 (1957).
- ⁸ Ziegler, K., and others, *Ann.* **511**, 13, 45, 64 (1934).
- ⁹ Wittig, G., Meyer, E. J., and Lange, G., *Ann.* **571**, 167 (1951).
- ¹⁰ Piotrovskii, K. B., and Ronina, M. P., *Doklady Akad. Nauk SSSR*, **115**, 737 (1957).
- ¹¹ Gilman, H., and Haubein, A. H., *J. Am. Chem. Soc.* **66**, 1515 (1944).
- ¹² Burgova, M. P., Korotkov, A. A., *Izvest. Akad. Nauk SSSR, Physics Series*, **14**, 482 (1950).
- ¹³ Pokrovskii, E. A., and Vol'kenshtein, M. V., *Doklady Akad. Nauk SSSR*, **95**, 301 (1954).

THE COPOLYMERIZATION OF ISOPRENE AND 1,3-BUTADIENE BY BUTYLLITHIUM *

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Up to now catalytic copolymerization with alkali catalysts has hardly been studied. Only a few papers have been published which give quantitative data¹⁻³. Judging by the values of the copolymerization constants, monomers differ very considerably in their reactivities. Monomers in which the double bond of the vinyl group is conjugated with the multiple bond of a nitrile or a carboxyl group have the greatest activity. The copolymerization of diene hydrocarbons under the action of basic catalysts has not been investigated as yet. It is known that in free radical (emulsion) polymerization these hydrocarbons have relatively similar activities⁴.

It seemed interesting to establish the relative reactivity of the diene hydrocarbons, isoprene and 1,3-butadiene, which differ by only a methyl group, in alkali-catalyzed copolymerization. Labeled atoms were used for determining the composition of the copolymers. For this we synthesized isoprene containing radioactive carbon, C¹⁴ (from acetylene-C¹⁴, prepared from BaC¹⁴O₃) by a modification of Favorskil's method⁵.

Copolymerization and separate polymerizations of isoprene and 1,3-butadiene were carried out in hexane solution with butyllithium at 50°, with a total monomer concentration of 2 moles/liter and a catalyst concentration of 0.0025 mole/liter. Butyllithium was synthesized by the known method⁶. The butyllithium solution was analyzed by the usual method with a double titration⁸.

Thoroughly purified and dried monomers and solvent were used for the polymerization. All operations of measuring out the products into the reaction ampules were carried out in a current of dry nitrogen and in a vacuum apparatus having a distributing comb (manifold). The reaction ampules consisted of two sections, separated by a wall and connected with a graduate tube. The solvent and monomers were placed in one section and the catalyst, a solution of butyllithium in hexane, in the other.

The wall in the ampule was broken with a glass plunger and the contents of the ampule mixed together rapidly. Polymerization was performed in a water thermostat at 50°. The polymerization rate was determined from the decrease in volume of the reaction solution.

The polymerization was stopped at different degrees of reaction by cooling the reaction ampule rapidly, then opening it and adding a small amount of ethyl alcohol (2 ml) to decompose the catalyst. The unreacted monomers and solvent were distilled from the ampule and the degree of reaction was determined by the weight of the polymer, dried at 60-80° (p = 2 mm Hg).

The copolymer compositions were determined by the radioactivity of the samples: as the standard we used polyisoprene-C¹⁴, whose relative activity was

* Reprinted from the *Proceedings of the Academy of Sciences, USSR (Physical Chemistry)*, 253-256 (1966); a translation by Consultants Bureau, Inc. of *Doklady Akad. Nauk SSSR*, 119, 982-5 (1966).

TABLE I
THE RELATION OF COPOLYMER COMPOSITIONS TO THE COMPOSITION
OF THE INITIAL MIXTURE AND THE DEGREE OF REACTION

Composition initial mixture, mole %		Copolymer comp. by radioactivity mole %		Conversion, %	Composition initial mixture mole %		Copolymer comp. by radioactivity mole %		Conversion, %
Isoprene	1,3-C ₄ H ₆	Isoprene	1,3-C ₄ H ₆		Isoprene	1,3-C ₄ H ₆	Isoprene	1,3-C ₄ H ₆	
51.1	48.9	43.7	56.3	84.6	20.7	79.3	6.6	93.4	40.2
49.0	51.0	27.0	73.0	14.5	19.8	80.2	9.5	90.5	64.5
48.7	51.3	28.3	71.7	25.2	20.9	79.1	8.0	92.0	11.9
52.2	47.8	28.7	71.3	13.4	78.9	21.1	57.5	42.5	42.3
51.1	48.8	31.9	68.1	35.4	69.7	30.3	54.4	45.6	16.8
49.0	51.0	34.5	65.5	69.5	78.0	22.0	63.0	37.0	50.8

expressed as the number of standard units in a sample of $\text{BaC}^{14}\text{O}_3$. The polymer samples were collected in small brass vessels (2 cm in diameter and 0.5 cm high), whose geometric position was fixed under the window of an end-window counter. The experimental results are given in Table I. The data obtained made it possible to calculate the copolymerization constants by the exact Mayo-Lewis integral Equation⁹, $\alpha = 0.47 \pm 0.03$ (for isoprene) and $\beta = 3.38 \pm 0.14$ (for 1,3-butadiene). Figures 1 and 2 give the curves calculated for the copolymer compositions and also the experimental points.

With the given initial monomer ratios, the copolymer compositions were calculated graphically by the known integral equation for copolymerization

$$\beta = \frac{\log \frac{B_0}{B} - \frac{1}{p} \log \frac{1 - p \frac{A}{B}}{1 - p \frac{A_0}{B_0}}}{\log \frac{A_0}{A} + \log \frac{1 - p \frac{A}{B}}{1 - p \frac{A_0}{B_0}}} \quad (1)$$

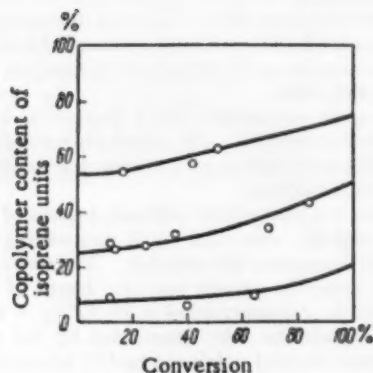


FIG. 1.—Calculated integral curves of the isoprene-1,3-butadiene system ($\alpha = 0.47$; $\beta = 3.38$).

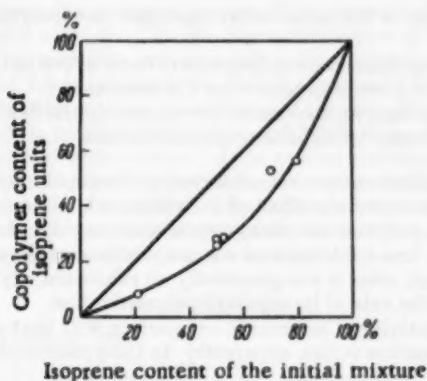


Fig. 2.—Copolymerization curve of the isoprene-1,3-butadiene system.

where $p = \frac{1 - \alpha}{1 - \beta}$, may be expressed as:

$$\log \frac{B_0}{B} = \frac{\alpha\beta - 1}{(\beta - 1)(\alpha - 1)} \log \frac{\frac{A}{B} - \frac{1}{p}}{\frac{A_0}{B_0} - \frac{1}{p}} - \frac{\beta}{\beta - 1} \log \frac{\frac{A}{B}}{\frac{A_0}{B_0}} \quad (2)$$

If the following criterion is introduced

$$\frac{A}{A_0} = x; \frac{B}{B_0} = y; \frac{\alpha\beta - 1}{(\beta - 1)(\alpha - 1)} = k_1; \frac{\beta}{\beta - 1} = k_2;$$

$$\frac{B_0}{A_0} \cdot \frac{1}{p} = k_3; k_4 = k_1 \ln(1 - k_3)$$

where A_0 and B_0 are the monomer concentrations at the initial moment and A and B are the monomer concentrations at the moment of terminating polymerization, then Equation (2) will appear as:

$$\log y + k_1 = k_1 \log \left(\frac{x}{y} - k_3 \right) - k_2 \log \frac{x}{y} \quad (3)$$

A graphic resolution of Equation (3) makes it possible to determine the magnitude $z = \frac{x}{y}$ for various values of y , i.e., to determine the required values A and B .

The experimental points lie quite well on the calculated curves, when one considers the permissible errors in measuring the monomers volumetrically.

Figure 3 gives the rate curves for the separate polymerization of isoprene and 1,3-butadiene and the copolymerization at a monomer ratio of 1:1.

It follows from the experimental data given that:

1. 1,3-Butadiene is the more active monomer in copolymerization ($\beta > 1$; $\alpha < 1$).
2. In separate polymerization, isoprene is more active as it polymerizes at a rate approximately 3 times greater than 1,3-butadiene.
3. In copolymerization, the rate of the reaction in the first stage corresponds to the rate of separate 1,3-butadiene polymerization.

An analogous phenomenon was observed in the copolymerization of styrene with 1,3-butadiene under the effect of butyllithium⁴. In separate polymerization, styrene was polymerized many times more rapidly than the diene. In copolymerization, first 1,3-butadiene was polymerized at the rate of its separate polymerization and, after it was practically all exhausted, styrene started polymerizing, also at the rate of its separate polymerization.

The higher reactivity of isoprene in comparison with that of 1,3-butadiene in separate polymerization is due, apparently, to the presence of a constant dipole

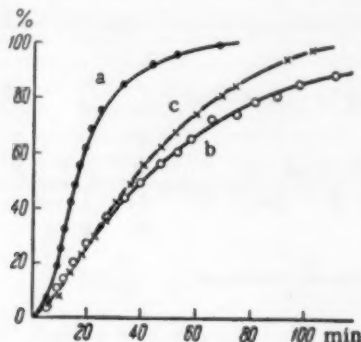
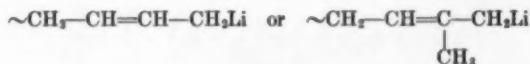


FIG. 3.—Polymerization rate curves $C_{\text{mon}} = 2$ moles/liter; $C_{\text{cat}} = 0.0025$ mole/liter. a) Isoprene, b) 1,3-butadiene, c) isoprene—1,3-butadiene (1:1).

moment in an isoprene molecule caused by the positive induction effect of the methyl group.

The phenomenon of the "inversion" of the monomer's activity in copolymerization cannot be explained on the basis of the ideas on the step mechanism of polymerization¹⁰. Regardless of the end unit in the growing polymer chain:



the probability of addition of each monomer molecule must be controlled by the activity of the monomer and its concentration in the solution. Thus, in our case the copolymer must be enriched in isoprene.

In order to explain the phenomenon of the "inversion" of the monomer's activity, the course of the reaction may be expressed as follows. In catalytic polymerization the active center is a dipole which reacts with the surrounding medium; if the rate at which the monomer reacts with the dipole, which could also be a metallo-organic compound, is relatively low, then the dipole would be surrounded by an envelope of polarized monomer molecules. The copolymer

composition and the polymerization rate would be determined by the monomer concentration in this envelope. In the copolymerization of isoprene with 1,3-butadiene, due to the relatively greater lability of the electron cloud and smaller steric hindrances of 1,3-butadiene molecules, the monomer envelope would apparently consist mainly of diene molecules. Therefore, the total rate corresponds to the separate polymerization rate of 1,3-butadiene and the copolymer composition is enriched in the latter. As in radical polymerization the active center has no charge and is not dipolar, no such envelope forms and the addition order of monomer molecules depends only on the concentration and relative activity of the monomers and free radicals at the ends of the growing chains and therefore the phenomenon of "inversion" does not occur.

REFERENCES

- ¹ Landler, J., *Compt. rend.* **230**, 539 (1950).
- ² Landler, J., *J. Polymer Sci.* **6**, 64 (1952).
- ³ Foster, F. C., *J. Am. Chem. Soc.* **72**, 1370 (1950).
- ⁴ Foster, F. C., *J. Am. Chem. Soc.* **74**, 2299 (1952).
- ⁵ Chesnokova, N. N. and Korotkov, A. A., *Theses of Repts. to the Ninth Conference on the General Problems of Chemistry and Physics of High Molecular Compounds* (Moscow, 1956), p. 32.
- ⁶ Orr, R. J. and Williams, H. L., *Can. J. Chem.* **30**, 108 (1952).
- ⁷ Favorskii, A. E., *Trans. Sess. Acad. Sci. USSR on Organic Chemistry* (Acad. Sci. USSR Press, 1939), p. 38. Korotkov, A. A., Mitsengender, S. P. and Rakova, G. V., *Coll. Repts. All-Soviet Conf. on the Use of Isotopes in Science and Industry* (Moscow, 1957).
- ⁸ Kochezhkov, K. A. and Talalaeva, T. V., "Synthetic Methods in the Field of Metallo-organic Compounds of Lithium, Sodium, Potassium, Rubidium, and Cesium" (Acad. Sci. USSR Press, 1949), pp. 26, 352.
- ⁹ Mayo, F. R. and Lewis, F. M., *J. Am. Chem. Soc.* **66**, 1594 (1944).
- ¹⁰ Ziegler, K. and Bahr, K., *Ber.* **61**, 253 (1928); Medvedev, S. S. and Abkin, A., *Trans. Faraday Soc.* **32**, 286 (1936).

THE BUTYLLITHIUM-INITIATED POLYMERIZATION OF 1,3-BUTADIENE *

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INTRODUCTION

The organolithium polymerization of isoprene (2-methyl-1,3-butadiene) has been studied in some detail. Hsieh and Tobolsky have reported that the polymer prepared in benzene or heptane had more than 90% *cis*-1,4-structure¹. Polyisoprenes prepared in ethers showed a change in stereochemistry to 3,4-, 1,2-, and *trans*-1,4-microstructures^{1,2}. Other research further studied the sensitivity of polymer stereochemistry to solvent and the specific organometallic initiator³. Although it was observed long ago⁴ that organolithium compounds cause the polymerization of butadiene, the stereochemistry of the polymer has been reported much less completely. The patent literature contains references⁵ in this area, and Russian researchers have studied the butyllithium-initiated polymerization of butadiene in the presence of ethers, oxygen, alcohols, and thio ethers⁶. This communication describes the polymerization of butadiene by butyllithium in *n*-heptane; it discusses the stereochemistry of the polymer obtained and the effect of catalyst and monomer concentration, polymerization temperature, and the presence of ethers on the details of polymer structure. The results obtained are compared with the reported data for the alkyllithium-initiated polymerization of isoprene.

EXPERIMENTAL

MATERIALS

In routine experiments C.P. butadiene (Matheson Co.) was distilled and determinant solutions prepared in *n*-heptane. Gas chromatography indicated a typical butadiene assay of 98 wt.-% and showed 1.2% of *trans*-2-butene and 0.4% each of isobutylene and 1-butene. Several experiments with a 99.6 wt.-% butadiene (Phillips Petroleum Co.) yielded polybutadienes with the same structure as that obtained with the C.P. material. Solutions were prepared in a dry box under nitrogen, and polymerizations were carried out in glass bottles. Solvents were reagent grade and distilled from lithium dispersions or sodium wire under nitrogen before use. Iso- and *n*-butyllithium were prepared in *n*-heptane according to the procedure of Gilman⁷ and *n*-butyllithium in *n*-heptane was also obtained from the Lithium Corp. of America. Experiments with the laboratory and commercial organolithium materials gave concordant results. *N*-Phenyl-2-naphthylamine was used as a polymer antioxidant, polymers were dried at 50° *in vacuo*, and inherent viscosities were determined in toluene at 20°.

* Reprinted from the *Journal of Polymer Science*, Vol. 42, pages 299-308 (1960).

POLYMER INFRARED ANALYSIS

The polymerization of butadiene can yield a polymer with three structural configurations resulting from the *cis*-1,4-, *trans*-1,4-, and 1,2-modes of monomer addition. The latter two structures show characteristic infrared absorption at 10.4 and 11.0 μ , respectively; the more difficult determination of the *cis*-1,4-structure has been achieved by various techniques. Richardson determined the *cis*-1,4-structure of thermally bulk polymerized butadiene by difference⁸. Binder used the absorption at 14.7 μ as a measure of *cis*-1,4-structure⁹, while Hampton used the absorption at 13.8 μ ¹⁰. Recently, Silas and co-workers have published a procedure in which an integrative technique, from 12.0 to 15.75 μ , is used for determining high levels of *cis*-1,4-structure¹¹.

Table I compares the results of the analysis by the various procedures of a typical polybutadiene prepared in the current research by *n*-butyllithium at 30°. The polybutadienes prepared in this work have been of theoretical unsaturation as indicated by iodine number determinations. Certain polymers gave slightly low iodine numbers, as would be expected for interference by catalyst residues and antioxidant. The last line of Table I shows good agreement between the nominal concentration of the solution and the sum of the concentrations for the various modes of addition. The various techniques give 48–58%

TABLE I
POLYBUTADIENE STRUCTURE BY VARIOUS INFRARED PROCEDURES

Procedure, %	Richardson ⁸	Binder ⁹	Hampton ¹⁰	Silas ¹¹
<i>trans</i> -1,4	48	58	52	48
<i>cis</i> -1,4	42	33	39	45
1,2	10	9	9	7
Nominal concn.	—	96	87	98

trans-1,4-, 33–45% *cis*-1,4-, and 7–10% 1,2-addition for the microstructure of this polybutadiene. The various analytical procedures are in general agreement, although the Binder and Hampton analyses appear to give higher values for *trans*-1,4 and lower for *cis*-1,4 than the other two. The structure of polybutadiene prepared by lithium metal initiation has been reported as 52% *trans*-1,4-, 35% *cis*-1,4-, and 13% 1,2-addition using the Binder infrared procedure¹², essentially identical to the structure we obtain using butyllithium and the same infrared procedure.

This research was concerned with testing the sensitivity of polymer microstructure to changes in polymerization conditions. We have used the Richardson infrared procedure to detect these changes. In studying the tables in the later sections, it should be recognized that this analytical procedure may yield somewhat higher values for *cis*-1,4-addition than the Binder and Hampton procedures. Spectra were determined for 0.5–2.0% polybutadiene solutions in carbon disulfide on a Baird Model B recording spectrophotometer; replicate determinations indicated a relative reproducibility of about 10% for the values of each of the various modes of addition.

RESULTS

Butadiene in *n*-heptane was readily polymerized by low concentrations of butyllithium. Polymers ranging from oils to rubbers were obtained, depending on reaction conditions. Typical polybutadienes showed 40–50% of *trans*-

TABLE II
BUTADIENE POLYMERIZATION AT DIFFERENT INITIATOR CONCENTRATIONS
(Butadiene 14 molal in *n*-heptane, 18 hours, 23°)

Concn. iso-BuLi, molal	Polymer microstructure, %			Conver- sion, %
	<i>trans</i> -1,4	1,2	<i>cis</i> -1,4	
0.002	39	9	52	40
0.005	40	9	51	55
0.009	40	10	50	60
0.014	40	9	51	60

and *cis*-1,4-structure and 5-10% 1,2-addition. Table II shows some characteristics of polymers obtained at different initiator concentrations. A sevenfold change in isobutyllithium concentration leaves the structure of the polymer unchanged.

Table III collects the results of experiments at constant isobutyllithium concentration and varied butadiene concentrations. The data show that well within the precision of the infrared analytical procedure polymer structure is insensitive to monomer concentration.

Polymer structure as a function of conversion level is shown in Table IV. Polybutadiene structure was found to be constant over the range studied.

TABLE III
POLYMERIZATION AT VARIED INITIAL BUTADIENE CONCENTRATIONS
(iso-BuLi 0.007 molal, *n*-heptane, 19 hours, 23°)

Concn. butadiene, molal	Concn. iso-BuLi mole-% on monomer	Conver- sion, %	Polymer microstructure, %		
			<i>trans</i> -1,4	1,2	<i>cis</i> -1,4
4	0.24	50	40	9	51
9	0.12	55	44	10	46
18	0.08	55	44	11	46
34	0.06	50	39	11	50

Both iso- and *n*-butyllithium yielded polybutadienes of the same structure, it will be noted, by comparing the data in Table IV with those in Table II and III.

Table V shows the structure of polybutadienes prepared by *n*-butyllithium initiation at temperatures from 4° to 80°. The data demonstrate that polymer microstructure was essentially constant over the range studied, consisting of approximately equal amounts of *trans*- and *cis*-1,4-structure with a small amount of 1,2-addition.

Korotkov has reported that the polymerization of butadiene by butyllithium in ethyl ether or 1,4-dioxane gave polymers with large amounts of 1,2-units⁶.

TABLE IV
POLYBUTADIENE STRUCTURE AT DIFFERENT CONVERSIONS
(Butadiene 7 molal, *n*-heptane, *n*-BuLi 0.007 molal, 23°)

Conversion, %	Polymer microstructure, %		
	<i>trans</i> -1,4	1,2	<i>cis</i> -1,4
5	44	9	47
10	46	9	45
20	47	9	44
60	46	9	45

TABLE V
POLYBUTADIENE PREPARED AT VARIOUS TEMPERATURES

Polymerization, temp.	Concn. butadiene, molal	Concn. <i>n</i> -BuLi, molal	Conversion, %	Polymer microstructure, %		
				<i>trans</i> -1,4	1,2	<i>cis</i> -1,4
4	2.0	0.006	55	47	9	44
30	4.0	0.006	40	48	10	42
39	2.0	0.006	40	47	8	45
65	3.9	0.005	100	42	10	48
80	3.9	0.007	95	47	11	42

We have investigated the sensitivity of butadiene polymer structure to the presence of ethers. Table VI shows the results of experiments carried out in the presence of small amounts of ethyl ether, tetrahydrofuran (THF) and methyl tetrahydrofuran. In all cases the molar concentration of ether present was greater than the butyllithium concentration. These polar reagents alter the course of polymerization to yield enhanced 1,2-polymer structure, and small equal amounts of *trans* and *cis* structure. An experiment was also performed in which butadiene was polymerized in the presence of a very large concentration of tetrahydrofuran. A 7-molal butadiene solution in tetrahydrofuran

TABLE VI
BUTADIENE POLYMERIZATION IN THE PRESENCE OF ETHERS
(0.5 VOLUME-% ON SOLUTIONS)
(Butadiene 9 molal, *n*-heptane, *n*-BuLi 0.007 molal, 23°)

	Ether			
	None	Ethyl ether	THF	Methyl THF
1,2-addition, %	10	29	51	46
<i>trans</i> -1,4, %	44	38	24	30
<i>cis</i> -1,4, %	46	33	25	24
Conversion, %	60	65	70	40

with 0.02 molal *n*-butyllithium was polymerized to 5% conversion at 23° and yielded a polybutadiene with 87% 1,2-addition, 7% *trans*-1,4- and 6% *cis*-1,4-structure.

The amount of 1,2-addition in polybutadiene prepared by sodium polymerization in bulk has been shown to be temperature dependent¹³ and suggests that in the present case the different modes of polymerization might be characterized by different rates. However, the constancy of polybutadiene struc-

TABLE VII
STRUCTURE OF POLYBUTADIENE FRACTIONS (ETHYL ETHER
EXTRACTION, 80 HOURS)

Polymer property	Soluble fraction	Insoluble fraction
% of original polymer	25	75
Content in fractions		
<i>trans</i> -1,4, %	44	39
1,2, %	11	10
<i>cis</i> -1,4, %	45	51
Inherent viscosity	3.75	4.44

ture over the wide temperature range studied in the current research (Table V) and the independence of polymer structure on conversion level (Table IV) show that this is not the case for the butyllithium polymerization of butadiene. This point was further strengthened by the fractionation experiment shown in Table VII. A polybutadiene of high inherent viscosity was extracted continuously by ethyl ether, and the soluble and insoluble fractions were then analyzed by infrared spectroscopy. The data in Table VII indicate that both fractions were composed of about 40% *trans*-1,4-, 50% *cis*-1,4-, and 10% 1,2-structural units. These fractionation results, in connection with the other evidence cited, suggest structural homogeneity during the entire polymerization for the butyllithium polymerization of butadiene.

DISCUSSION

The data presented here demonstrate that in *n*-heptane the polymerization of butadiene by butyllithium yields a polymer with large amounts of both *cis* and *trans*-1,4-structure and about 10% 1,2-addition. We feel that the detailed microstructure lies within the range indicated by Table I, that is, 48–58% *trans*-1,4-, 33–45% *cis*-1,4-, and 7–10% 1,2-addition. This polymer structure was independent of catalyst and monomer concentration over the range studied and showed a remarkable constancy, independent of polymerization temperature, in experiments from 4 to 80°. Also, polymer structure seemed to be independent of the polymerization conversion to which the reaction had been carried. Small amounts of ethers change polymer structure very markedly, increasing the amount of 1,2-addition to a great extent. Polymerization in tetrahydrofuran yielded a polymer with more than 80% 1,2-addition and small and approximately equal amounts of *cis* and *trans*-1,4-structure.

It is interesting to compare these results obtained with butadiene with those reported for the analogous polymerization of isoprene. Isoprene yields a polymer with 91% *cis*-1,4- and 9% 3,4-structure when polymerized in heptane or benzene by butyllithium². We note, then, that the change on going from isoprene to butadiene involves a change in the normal mode of addition from a highly selective and specific *cis*-1,4-stereochemistry to a predominantly 1,4-mode of enchainment, but with large amounts of both *cis* and *trans* structure. The polymerization of isoprene in tetrahydrofuran by butyllithium yields a polyisoprene with 69% 3,4- and 31% 1,2-addition³; the polymerization of butadiene in the same ether solvent gives a polybutadiene with 87% 1,2-addition.

Stearns and Forman have suggested that the stereospecificity of isoprene polymerization by alkylolithium in hydrocarbon solvents is due to a *cis* coordination complex of the monomer in the *cis* configuration with the C—Li bond of the growing polymer^{14a}. They further postulated that this coordination complex undergoes a rearrangement to form a six-membered cyclic activated complex during monomer addition. Raman spectra studies have indicated that the *cis* configuration of isoprene is more stable than the *trans* form by 900 cal/mole, and the equilibrium mixture at 50° contains 85% of the *cis* isomer¹⁵. The profound effect of ethers on polymer structure was ascribed to their coordination as Lewis bases with the terminal lithium atoms, thus interfering with the formation of the proposed cyclic activated complex^{14a}.

The highly polarized C—Li bond of the growing polymer in hydrocarbon solvent seems attractive as a locus for association, coordination, or solvation by both monomer and alkylolithium. Alkylolithiums have been demonstrated to be highly associated in organic solvents^{16,17}. Further, it seems probable

that the configuration of the innermost complexed diolefin in the coordinate complex, if many diolefin molecules are involved, would control the steric course of the incorporation of the next monomer unit into the growing polymer chain. Raman spectroscopy has indicated even greater differences in the relative stabilities of the *cis* and *trans* configurations of 1,3-butadiene than have been reported for isoprene. In this case, it was estimated that the equilibrium mixture contains less than 4% of the *cis* configuration at room temperature¹⁸. The planar *trans* form has been reported to be more stable than the *cis* form¹⁹ by about 2000 cal/mole. It was calculated that even at 1500° K only 46% of the molecules exist in the *cis* configuration¹⁹. Despite these reported differences in the stabilities of the *cis* and *trans* rotational isomers of butadiene, failure to observe a highly selective polymerization to a *trans*-1,4-polymer indicates that in the butyllithium-initiated polymerization in heptane solvent such energetic differences do not control the course of polymerization. The independence of polybutadiene structure on polymerization temperature contrasts with the reported observations that increasing polymerization temperature with isoprene yields more 3,4- and *trans*-1,4-structure^{16b}. Stearns and Forman have

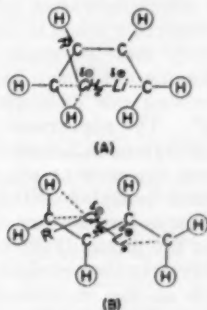


Fig. 1.—Schematic representation of the *cis* and *trans* coordination complexes of butadiene with the growing polymer chain: (A) *cis* complex; (B) *trans* complex.

calculated that the energy of activation for 3,4-addition is 2010 cal/mole greater than that for *cis*-1,4-addition, in the isoprene case^{16b}. It would appear that for butadiene, the coordination complex must involve large numbers of butadiene molecules complexed in the *cis* fashion. Thus, it would appear necessary to postulate that the steric requirements and energy of both the *cis* and *trans* configurations of butadiene, indicated schematically in Figure 1, are not very different. In effect, the polymer C—Li bond must convert molecules in the *trans* configuration in solution into *cis* molecules in the coordination complex. An alternate, to us less attractive, possibility would be that the coordination complex contains the energetically more favorable *trans* configuration primarily but that *cis* structures are formed as the diolefin is incorporated into the polymer chain. These observations would indicate that the isoprene *cis*-1,4 coordination complex—the isoprene analog of Figure 1A—(which must be much more stable than the *trans* form) is of appreciably lower stability than both the *cis* and *trans*-1,4-complexes of butadiene. It has been observed that the butadiene-solid cuprous chloride complex is more stable than the corresponding isoprene complex²⁰. Thus, in the polymerization of isoprene, re-

action temperature is very important in determining polymer structure while butadiene is essentially insensitive to this variable. The invariance of polybutadiene structure over the temperature range studied may be due to similar enthalpy and entropy values for the *cis* and *trans* coordinate complexes, or to a fortuitous compensation between different values and the relative concentration of the *cis* and *trans* conformations available in solution at the various temperatures. Figure 1 is intended to indicate that dual-site coordination is necessary for steric control of 1,4-addition. Partly cationic lithium is suggested as one locus of control by association with an electron-rich diene carbon atom. The partly anionic carbon atom of the C—Li bond may coordinate either with a hydrogen atom, an electron-deficient diene carbon, or with both. Stereospecificity thus operates during synchronous bond making and breaking during monomer addition. Chain growth may occur in complicated alkylolithium-monomer soluble aggregates, called "micelles" by Korotkov⁶, and involve several polymer chains at the same time.

The insensitivity of polybutadiene structure to butyllithium concentration indicates that butadiene monomer coordinates with the C—Li bond of the growing chain more effectively than does alkylolithium; again, these results contrast with the isoprene case where increasing alkylolithium concentration decreases the amount of *cis*-1,4-structure found in the polymer^{14b}. Ethers or thio ethers⁶ coordinate so effectively that the mode of monomer coordination is changed to the 1,2-type. Kinetic data have been cited as evidence for the formation of a complex involving one molecule of *n*-butyllithium and two molecules of tetrahydrofuran²¹. The appearance of colored species during the alkylolithium polymerization of styrene in benzene and ethers indicates that, in solvents of good ionizing power, the growing polymer chain can be sufficiently solvated so as to yield colored benzyl ion-lithium cation ion pairs^{21,22}. In effect, organolithium compounds in the presence of Lewis bases, such as ethers, are solvated to an extent that the primarily covalent C—Li bond becomes essentially ionic and then behaves in its reactions very much like more ionic organoalkali compounds such as the organosodium compounds. It would then appear that the uniqueness of organolithium (or lithium metal) catalysis in aliphatic hydrocarbon solvents in yielding diolefin polymers with large amounts of 1,4-structure may be due to the covalent structure of organolithium compounds²³, the small size of the lithium atom, its suitable polyvalence, and the ease of polarization to form diolefin coordination complexes.

In summary, then, we would visualize the C—Li bond of the growing polymer chain to be involved in a reversible equilibrium in some aggregate structure involving butadiene molecules, and fairly insensitive to association with organolithium compounds, and that within this complex polymer growth occurs. It would seem that the butadiene in the complex involves large amounts of both *cis* and *trans* configurations and that this distribution is insensitive to variations in temperature.

SYNOPSIS

The structure of polybutadiene prepared by butyllithium initiation in *n*-heptane has been studied by four infrared procedures. A typical polymer prepared by *n*-butyllithium at 30° gave values of 48–58% *trans*-1,4-, 33–45% *cis*-1,4-, and 7–10% 1,2-addition, depending on the particular analytical technique used. Iso- or *n*-butyllithium gave polybutadienes with the same structure. Polymer stereochemistry is independent of monomer and initiator concentration and extent of polymerization conversion. Polybutadiene prepared

in experiments from 4 to 80° showed the same structure. Polymerization in the presence of small amounts of ethers yields 1,2-addition as the major structural unit. These results contrast with the reported behavior of isoprene in similar polymerizations where increasing alkylolithium concentration and reaction temperature increase the amount of 3,4-addition and decrease the amount of *cis*-1,4-structure. Possible reaction routes for these transformations are discussed.

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REFERENCES

- ¹ Haieh, H. and Tobolsky, A. V., *J. Polymer Sci.* **25**, 245 (1957).
- ² Haieh, H., Kelley, D. J. and Tobolsky, A. V., *J. Polymer Sci.* **26**, 240 (1957).
- ³ Morita, H. and Tobolsky, A. V., *J. Am. Chem. Soc.* **79**, 5853 (1957).
- ⁴ Ziegler, K. and Jakob, L., *Ann. Chem. Liebigs* **511**, 45 (1934).
- ⁵ Foster, F. C. (Firestone Tire & Rubber Co.) *Australian* **222**, 573 (Oct. 29, 1959).
- ⁶ Korotkov, A. A., *Inter. Symp. Macromolecular Chem., Prague*, Sept. 1957, Paper 66; *Angew. Chem.* **70**, 85 (1958). Kropachev, V. A., Dolgoplosk, B. A. and Nikolaev, N. L., *Doklady Akad. Nauk S.S.S.R.* **115**, 516 (1957); *Chem. Abstr.* **52**, 3386 (1958).
- ⁷ Gilman, H., Langham, W. and Moore, F. W., *J. Am. Chem. Soc.* **62**, 2333 (1940).
- ⁸ Richardson, W. S., *J. Polymer Sci.* **13**, 229 (1954).
- ⁹ Binder, J. L., *Anal. Chem.* **26**, 1877 (1954).
- ¹⁰ Hampton, R. R., *Anal. Chem.* **21**, 923 (1949).
- ¹¹ Silas, R. S., Yates, J. and Thornton, V., *Anal. Chem.* **31**, 529 (1959).
- ¹² Foster, F. C. and Binder, J. L., "Handling and Uses of the Alkali Metals", ACS Monograph No. 19, 26 (1957).
- ¹³ Kolthoff, I. M., Lee, T. S., and Mairs, M. A., *J. Polymer Sci.* **2**, 220 (1947).
- ¹⁴ (a) Stearns, R. S. and Forman, L. E., 134th Am. Chem. Soc. meeting, Sept., 1958, Abstr. 12U; (b) *idem*, *J. Polymer Sci.* **41**, 351 (1959).
- ¹⁵ Nikitin, V. N. and Yakovleva, T. V., *Zhur. Fiz. Khim.* **28**, 697 (1954); *Chem. Abstr.* **49**, 5906 (1955).
- ¹⁶ Coates, G. E., "Organometallic Compounds," p. 7, Methuen, London, 1956.
- ¹⁷ Piotrovskii, K. B. and Ronina, M. P., *Doklady Akad. Nauk S.S.S.R.* **115**, 737 (1957).
- ¹⁸ Richards, C. M. and Nielsen, J. R., *J. Opt. Soc. Am.* **40**, 438 (1950).
- ¹⁹ Aston, J. G., Seass, G., Woolley, H. W. and Brickwedde, F. G., *J. Chem. Phys.* **14**, 67 (1946).
- ²⁰ Gilliland, E. R., Bliss, H. L. and Kip, C. E., *J. Am. Chem. Soc.* **63**, 2088 (1941).
- ²¹ O'Driscoll, K. F. and Tobolsky, A. V., *J. Polymer Sci.* **35**, 259 (1959).
- ²² Welch, F. J., *J. Am. Chem. Soc.* **81**, 1345 (1959).
- ²³ Rogers, M. T. and Young, A., *J. Am. Chem. Soc.* **68**, 2748 (1946).

COMPLEX FORMATION AND CHAIN STRUCTURE IN THE POLYMERIZATION OF DIVINYL WITH BUTYLLITHIUM *

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It has been established by a number of studies¹⁻³ that the chain structure in the catalytic polymerization of monoolefins and dienes is determined to a large degree by the nature of the catalytic complex, participating in the polymerization process. Also it was shown that the initial catalytic complex bears a direct relationship to each elementary act of the chain growth.

The isolation of organolithium compounds in the pure state is associated with great experimental difficulties. Together with the formation of the organometal compounds the possibility of a complex mixture of their oxidation products being formed is not excluded. To elucidate the influence of the indicated oxidation products on the chain structure in the polymerization of butadiene it seemed expedient to investigate the influence of oxygen.

As the result of the investigation made by us it was established that in the polymerization of 1,3-butadiene with organolithium compounds the introduction of comparatively small amounts of oxygen into the system leads to a substantial increase in the number of 1,2 units in the polybutadiene at the expense of a reduction in the number of 1,4 units. The addition of either alcohol or phenol exerts a similar influence on the structure of the polymeric chain (Table 1).

In principle the results obtained are of interest in the sense that they show the need for protecting the system from the entrance of oxygen when the problem is to synthesize 1,3-butadiene polymers with the maximum amount of 1,4 units in the chain. The influence of oxygen on the polybutadiene structure is apparently due to the formation of oxygen-containing products, which form complexes with organolithium compounds.

A similar effect is shown by dialkyl monosulfides, the influence of which was studied by us in detail. The effect of adding dimethyl, dipropyl and diisopropyl sulfides on the structure of the polybutadiene chain when the polymerization was done in the absence of oxygen was studied.

The data, obtained when butadiene was polymerized with butyllithium, reveal that dialkyl sulfides substantially increase the amount of 1,2 units in the chain and, in the case of dimethyl sulfide, the amount of 1,2 units is increased from 12 to 68% (Table 2).

From the data in Table 2 it can be seen that the influence of the dialkyl sulfide decreases with increase in the size of the alkyl radical. Earlier⁴ we had shown with butyllithium the ability of organolithium compounds to form com-

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TABLE 1

POLYMERIZATION OF 1,3-BUTADIENE WITH BUTYLLITHIUM AT 50° IN PETROLEUM ETHER SOLUTION IN THE PRESENCE OF ADDED OXYGEN, ALCOHOL OR PHENOL

Exp. No.	Additive	Butyllithium concentration	Concentration of additive	% of 1,2 units in the polybutadiene
		mole % on the monomer		
1	Without additive	0.040	—	12
2		0.055	—	11
3		0.056	—	10
4		0.060	—	10
1	Oxygen	0.050	0.018	32
2		0.050	0.037	21
3		0.057	0.037	43
4		0.057	0.037	33
5		0.060	0.011	26
6		0.130	0.011	29
1	Lithium benzylate*	1.36	5.30	39
2		1.36	5.30	37
1	Lithium phenolate*	0.15	5.79	35
2		0.15	5.79	33

* The benzylate and phenolate are shown, since the reaction of butyllithium with hydroxyl-containing additives leads to the formation of these substances even before the monomer is introduced into the system.

plexes with dimethyl sulfide. The insoluble complex obtained here had the composition

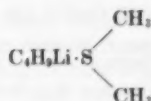
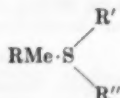


TABLE 2

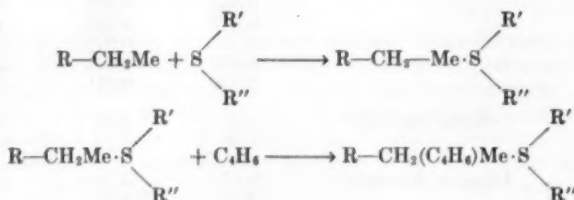
POLYMERIZATION OF 1,3-BUTADIENE WITH BUTYLLITHIUM AT 50° WITH ADDITIONS OF DIALKYL SULFIDES IN PETROLEUM ETHER SOLUTION

Exp. No.	Name of additive	Butyllithium concentration	Concentration of additive	% of 1,2 units in the polybutadiene
		mole % on the monomer		
1	Without additive	0.040	—	12
2		0.060	—	10
3		0.30	—	11
4		0.30	—	12
1	Dimethyl sulfide	0.14	61.74	62
2		0.19	82.0	68
1	Dipropyl sulfide	0.66	0.202	29
		0.22	2.49	31
1	Diisopropyl sulfide	0.28	57.3	28
		0.28	57.3	25

In general form such compounds can be written as



where Me is an alkali metal, and R, R' and R'' are alkyl radicals. Although it is probable that complexes of greater complexity than those isolated by us can participate in the polymerization process, the influence of complex-forming additions on the chain structure can be depicted as being in accord with the representations of Ziegler⁵ that the polymerization process is a sequence of organometallic syntheses. For the given case this scheme can be depicted as follows:



In view of the fact that the complex-forming additive is bound directly to the metal of the organometallic compound, it exerts an influence on the character of the carbon-metal bond during the whole process of forming the chain and in that way it exerts an influence on the structure of the polymer.

REFERENCES

- ¹ Morton, A., *Ind. Eng. Chem.* **42**, 1488 (1950); *J. Am. Chem. Soc.* **69**, 1675 (1947).
- ² Ziegler, K., Holskamp, E., Briel, A., and Martin, H., *Angew. Chem.* **67**, 541 (1955).
- ³ Natta, G., *Makromol. Chem.* **16**, 213 (1955).
- ⁴ Dolgoplosk, B. A., Kropachev, V. A., and Nikolaev, N. I., *Doklady Akad. Nauk SSSR*, **110**, 789 (1956).
- ⁵ Ziegler, K., et al., *Ann.* **473**, 57 (1928).

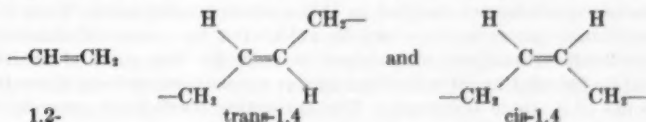
INFRARED ANALYSIS OF BUTADIENE POLYMERS *

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CONTRIBUTION FROM THE LABORATORY OF THE VERB. CHEM. WERKE
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The quantitative infrared spectroscopic determination of isomeric structural units in rubbery polymers, or generally speaking, the determination of the isomer ratio in any technical mixture (e.g. mixed *o*-, *m*- and *p*-diethylbenzenes) often presents difficulties because the needed calibration substances for determination of the extinction coefficients can only be prepared or acquired under considerable preparative efforts or sacrifice in time. Accordingly a procedure has been worked out whereby pure calibration substances are not needed; notably this new procedure is better adapted to the spectroscopic behavior of rubbery polymers than are the currently used methods.

Polybutadiene consists of three different components, i.e., structural units which together account for about 90 per cent of the polymer. With the cur-



rently used procedure the reference extinction coefficients for the quantitative infrared spectroscopic determination of these isomeric units are established by use of model olefins whose configurations are identical with the expected component units of the polymer. These values then are applied to the polybutadiene^{1-3, 7} high polymer. This procedure depends on the unproven assumption that the extinction coefficients of certain wave bands of the olefins are also valid for high molecular weight polybutadiene. In the first place calibration substances which are insufficiently purified³ may lead to misinterpretations but furthermore, the assumption that the extinction coefficients of specific olefin bands are applicable to high polymer analysis obviously is unreliable.

More serious difficulties occur with the determination of the *cis*-1,4 content because the extinction coefficient of the band† for this unit, which lies around 680 cm⁻¹, is very small and to date polymer samples with high *cis*-1,4 content were not available. According to the currently used method this component is determined either as a difference (whereby frequently the degree of unsaturation is assumed to be 100 per cent, which for most polymer types is incorrect), or the *cis*-1,4 fraction is determined by means of the 680 cm⁻¹ band. With the latter method¹ the measured values sometimes are corrected on a purely empirical basis up to 1:6. In the case of a butadiene-styrene copolymer this determination leads to large errors, because styrene shows a strong absorption band at 700 cm⁻¹.

* From an article in *Zeitschrift für analytische Chemie* Vol. 170, pages 132-47 (1959), translated for RUBBER CHEMISTRY AND TECHNOLOGY by FRANK WIDMER.

† A referee has pointed out to RUBBER CHEM. AND TECHNOL. that the band for 1,4-*cis* units usually occurs at about 735 cm⁻¹ and that high *cis*-1,4 polymers now are widely available.

The currently used method is based on the argument that the absorbance E of an analysis band is obtained according to Equation (1):

$$E = \log \frac{I_0}{I} \quad (1)$$

I_0 = Radiation intensity which passes through the solvent; I = Radiation intensity which passes through the solution.

Compensated double beam instruments accordingly use the value 100 in place of I_0 if the intensities are recorded as per cent transmission. The value E which is determined at wave length λ is formulated as follows:

$$E_\lambda = (\epsilon_\alpha^\lambda \cdot C_\alpha + \epsilon_\beta^\lambda \cdot C_\beta + \epsilon_\gamma^\lambda \cdot C_\gamma + \dots) d \quad (2)$$

ϵ^λ = Extinction coefficient of the i th component at position λ ; C_i = Concentration of the i th component; d = Cell thickness in cm.

The wave length λ is chosen in such a way that all extinction coefficients except one become as small as possible, i.e. an analysis band is (established) evaluated.

Now the absorbance values are determined from as many bands as there are components in the system, whereby (if possible) for a certain wave length the extinction coefficient value of one component must dominate numerically. A series of equations are created in this manner analogous to Equation (2). The individual concentrations can be calculated by means of determinants. The quantitative analysis of polymer isomers by this method therefore is achieved by calculating all individual isomer concentrations from the extinction coefficients of a single spectrum. The extinction coefficients are valid for all concentrations, if the Lambert-Beer law is applicable.

Our investigations have shown that it is of advantage to determine the absorbance values by a modified base line procedure. In this connection the meaning of I_0 in Equation (1) has been changed. I_0 now corresponds to the radiation intensity which is transmitted by all components with the exception of the component whose absorption at wave length λ is under investigation (the solvent is already compensated for). The consequence of this mode of evaluation for the extinction coefficients is as follows:

1. In Equation (2) all the extinction coefficients except one become zero.
2. The evaluation is not disturbed by foreign substances as long as they have no band in the range of the analysis band and provided that the background tangent is drawn according to certain specifications (see below).
3. The extinction coefficients are concentration dependent⁶ and except for special cases they have to be corrected accordingly.

DETERMINATION OF EXTINCTION COEFFICIENTS

For the determination of extinction coefficients of pure components of a mixture it is advisable to calculate first the purely operational extinction coefficients. According to Equation (3) they are obtained from the extinction values of specific analysis bands which were determined by the base line procedure and from the total concentration c_0 of the mixture.

$$\frac{E_1}{c_0 \cdot d} = \epsilon_1 \quad (3)$$

E_1 = absorbance of component 1; ϵ = Calculated extinction coefficient of component 1; c_g = Total concentration in moles per liter.

This value ϵ_1 is related as follows to the actual extinction coefficient ϵ_1^0 of component 1:

$$\epsilon_1 = \epsilon_1^0 \cdot x \quad (4)$$

x = mole fraction of component 1 in mixture 1.

For the case of a binary mixture the same relationships are valid for the extinction coefficient of the second component of the same mixture spectrum:

$$\epsilon_2 = \epsilon_2^0 \cdot x_2 = \epsilon_2^0 \cdot (1 - x) \quad \text{where } x + x_2 = 1. \quad (4a)$$

For the determinations of the coefficients of the pure substances (ϵ_i^0) in binary mixtures still a second mixture of a different quantitative composition is needed. Here accordingly we write for component 1:

$$\epsilon_1' = \epsilon_1^0 \cdot y \quad (5)$$

y = mole fraction of component 1 in mixture 2 and for the second component:

$$\epsilon_2' = \epsilon_2^0 \cdot (1 - y) \quad (5a)$$

This gives 4 equations with 4 unknowns (ϵ_1^0 , ϵ_2^0 , x and y) and 4 experimentally determined quantities (ϵ_1 , ϵ_2 , ϵ_1' and ϵ_2') and in addition to these the 2 total concentrations c_g and c_g' . From this set of equations not only the per cent contents x and y , but also the unknown extinction coefficients of the pure components of the mixture can be calculated by means of determinants. For a binary system the following equations are obtained:

$$x = \epsilon_1 \frac{\epsilon_2' - \epsilon_2}{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'} = \epsilon_1 \begin{vmatrix} 1 & \epsilon_2 \\ 1 & \epsilon_2' \\ \epsilon_1 & \epsilon_2 \\ \epsilon_1' & \epsilon_2' \end{vmatrix} \quad (6a)$$

resp.

$$1 - x = \epsilon_2 \frac{\epsilon_1 - \epsilon_1'}{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'};$$

$$y = \epsilon_1' \frac{\epsilon_2' - \epsilon_2}{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'} = \epsilon_1' \begin{vmatrix} 1 & \epsilon_2 \\ 1 & \epsilon_2' \\ \epsilon_1 & \epsilon_2 \\ \epsilon_1' & \epsilon_2' \end{vmatrix} \quad (6b)$$

resp.

$$1 - y = \epsilon_2' \frac{\epsilon_1 - \epsilon_1'}{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'};$$

$$\epsilon_1^0 = \frac{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'}{\epsilon_2' - \epsilon_2} = \begin{vmatrix} \epsilon_1 & \epsilon_2 \\ \epsilon_1' & \epsilon_2' \\ 1 & \epsilon_2 \\ 1 & \epsilon_2' \end{vmatrix} \quad (6c)$$

$$\epsilon_2^0 = \frac{\epsilon_1 \epsilon_2' - \epsilon_2 \epsilon_1'}{\epsilon_1 - \epsilon_1'} = \begin{vmatrix} \epsilon_1 & \epsilon_2 \\ \epsilon_1' & \epsilon_2' \\ \epsilon_1 & 1 \\ \epsilon_1' & 1 \end{vmatrix} \quad (6d)$$

For a three-component system 3 samples of different quantitative compositions are needed, in which no linear combinations shall occur.

Notation of the individual quantities:

Actual extinction coefficient	Component 1 ϵ_1^0	Comp. 2 ϵ_2^0	Comp. 3 ϵ_3^0
Mole fraction in mixture I	x	y	$z = 1 - x - y$
Mole fraction in mixture II	a	b	$c = 1 - a - b$
Mole fraction in mixture III	n	p	$m = 1 - n - p$
Calculated extinction coefficients			
In mixture I	ϵ_1	ϵ_2	ϵ_3
In mixture II	ϵ_1'	ϵ_2'	ϵ_3'
In mixture III	ϵ_1''	ϵ_2''	ϵ_3''

These notations can be used—quite similar to binary mixtures—to write the following solutions (expressed in determinants) for a three-component system:

$$\epsilon_1^0 = \frac{\begin{vmatrix} \epsilon_1 & \epsilon_2 & \epsilon_3 \\ \epsilon_1' & \epsilon_2' & \epsilon_3' \\ \epsilon_1'' & \epsilon_2'' & \epsilon_3'' \end{vmatrix}}{\begin{vmatrix} 1 & \epsilon_2 & \epsilon_3 \\ 1 & \epsilon_2' & \epsilon_3' \\ 1 & \epsilon_2'' & \epsilon_3'' \end{vmatrix}} \quad (7a)$$

$$\epsilon_2^0 = \frac{\begin{vmatrix} \epsilon_1 & \epsilon_2 & \epsilon_3 \\ \epsilon_1' & \epsilon_2' & \epsilon_3' \\ \epsilon_1'' & \epsilon_2'' & \epsilon_3'' \end{vmatrix}}{\begin{vmatrix} \epsilon_1 & 1 & \epsilon_3 \\ \epsilon_1' & 1 & \epsilon_3' \\ \epsilon_1'' & 1 & \epsilon_3'' \end{vmatrix}} \quad (7b)$$

and

$$\epsilon_3^0 = \frac{\begin{vmatrix} \epsilon_1 & \epsilon_2 & \epsilon_3 \\ \epsilon_1' & \epsilon_2' & \epsilon_3' \\ \epsilon_1'' & \epsilon_2'' & \epsilon_3'' \end{vmatrix}}{\begin{vmatrix} \epsilon_1 & \epsilon_2 & 1 \\ \epsilon_1' & \epsilon_2' & 1 \\ \epsilon_1'' & \epsilon_2'' & 1 \end{vmatrix}} \quad (7c)$$

The quantitative investigation of the 3 mixtures results in the following relationships for the mole fractions of the 9 components:

$$x = \frac{\epsilon_1}{\epsilon_1^0} \quad y = \frac{\epsilon_2}{\epsilon_2^0} \quad z = \frac{\epsilon_3}{\epsilon_3^0} \quad (8a)$$

$$a = \frac{\epsilon_1'}{\epsilon_1^0} \quad b = \frac{\epsilon_2'}{\epsilon_2^0} \quad c = \frac{\epsilon_3'}{\epsilon_3^0} \quad (8b)$$

$$n = \frac{\epsilon_1''}{\epsilon_1^0} \quad p = \frac{\epsilon_2''}{\epsilon_2^0} \quad m = \frac{\epsilon_3''}{\epsilon_3^0} \quad (8c)$$

This method can be generalized and extended to systems with n components. Attention should be called to the following requirement: an extinction coefficient has to be calculated for every one of the n components in each of the n mixtures.

For practical reasons the number n should not exceed 3 or 4; otherwise the inevitable experimental errors would introduce too many errors and consequently give false results. However, the errors probably would not exceed those of the older method, because the number of data which are needed for one determination is about the same for both methods (compare with the experimental part).

EXPERIMENTAL AND PRACTICAL EVALUATION PROCEDURE

Preparation of the solutions.—It is necessary to correct the test data in Equations (4–8). Since the extinction coefficients which are obtained by the base line procedure as a rule depend on the concentration⁶, the data have to be reduced to a standard which is reproducible. For this reason the concentrations of the stock solutions of the polymer samples are chosen in such a manner that the band peaks of the 1,2 or 1,4-*trans* structural units will show a transmission of 20–30 per cent. For a given cell thickness of 0.045 cm this corresponds to a butadiene structural unit ($54.1 \text{ g} = 1 \text{ g mol. wt.}$) concentration of 0.1–0.15 *M*. A solution of this concentration is prepared in carbon disulfide. From this stock solution a dilution series is prepared and its calculated extinction coefficients are linearly extrapolated to zero concentration ($c = 0$).

Equations (4–8) are perfectly valid for these extrapolated ϵ -values. This procedure has an advantage, because the experimental errors of the individual measurements can be kept at a minimum by averaging the data graphically. Coincidentally the deviations of the test data from the straight line curve permit judgment to be passed on the quality of the data. It should be mentioned that for very small concentrations ($c < 0.05 \text{ M}$) where the band peak is small the errors may be significant, whereas at large concentrations ($c > 0.15 \text{ M}$) interferences of unknown origin may cause deviations.

Since in the case of polybutadiene the sum of the structural units in question is about 90 per cent, it was considered necessary to determine the total unsaturation of the isomers separately. This was achieved by means of the iodine monochloride method⁷ which yields the true concentration of the sum of the isomers, from which the degree of unsaturation can be calculated as long as the sample weight is known.

This procedure provides still another advantage, especially for the analysis of butadiene copolymers. Since the determination of the unsaturation in a styrene-butadiene-copolymer does not pertain to polystyrene, the system is at most a three-component system. The styrene absorption bands are measured and evaluated separately.

Fixation of the spectrum background by the modified base line procedure.—A spectrum always consists of several bands. The band to be measured may be related with the other bands as follows:

- 1) The band to be measured lies entirely free. The other bands are spaced farther apart from the band in question.
- 2) Foreign bands occur in close proximity to the band under measurement (about $15\text{--}100 \text{ cm}^{-1}$) and this results in a partial superimposition. Here 2 cases may be shown: 2a) Only one interference band occurs; 2b) An interference band occurs on both sides of the band under measurement.

Case (1) is evaluated quite normally by drawing a tangent. In case (3) an evaluation can only be performed in exceptional cases, because the uncertainty is too great. Such bands cannot be determined with the old method either.

Case (2a) occurs with polybutadiene for the two 1,2-bands (910 and 995 cm^{-1}) as soon as the sample contains *trans* fragments (970 cm^{-1}). Case (2b) on the other hands is valid for the 1,4-*trans* component in the presence of 1,2-polymers. These 2 cases have been reconstructed and investigated with 1-octene and 1,4-dibromo-2-*trans*-butene. The concentration of the interference component (*trans* compound) was varied over a wide range while the octene concentration was kept constant and vice versa. In these experiments the concentrations of the octene and the dibromobutene, respectively, except for an experiment with median values, was at first chosen very small and then very large. The evaluation of the 6 experimental series was performed by 3 different methods:

1) A base line was drawn which was a tangent over an appreciable range of the spectrum. This base line can be drawn relatively easily for polybutadiene within the mentioned concentrations. In our experiments the straight line touched the spectrum at 880 and 1030 cm^{-1} .

2) The minima on both sides of the band under measurement were used as tangent points.

3) The I_0 values which were obtained according to (1) and (2) were averaged (modified base line procedure).

Table I shows that by the third method the deviations are not too large for most cases. However, for case (2b), under extreme conditions, large deviations may occur (They may perhaps be traced back to a small band, which the octene used showed at 970 cm^{-1}). Although these deviations are appreciably noticeable for small 1,4-*trans* values, in many cases it appears desirable to carry the corrections even further. Finally, it should be mentioned, that as with the older method (Equation 2) small quantities can only be detected only vaguely because of the uncertainty of the corrections.

Quantitative investigations of binary and ternary olefin mixtures.—The new method offers essentially 2 variations for the quantitative determination of isomers.

1) The determination of the ϵ^0 -values has already been described: a dilution series is prepared, the calculated extinction coefficients are extrapolated to $c = 0$, and the true extinction coefficients ϵ_i^0 or the mol fractions, respectively, of the individual components are determined by mathematical coupling of the relationships which prevail for binary or ternary systems, respectively.

2) In case the ϵ^0 values already exist, then also the per cent concentrations can be determined directly by means of Equations (4) or (8). Furthermore, this method offers the advantage that one component of the mixture may be determined indirectly from the difference.

In order to check the practicality and correctness of this method and to consolidate the results obtained, the two quantitative evaluation procedures described were checked on examples of low molecular weight binary and ternary olefin mixtures.

For the investigation of a *binary system* 1-octene and *trans*-1,4-dibromo-2-butene were used. By employing pure substances the following maximum extinction coefficients were extrapolated to $c = 0$:

$$\text{1-octene: } \epsilon_1^0 = 148 \frac{1}{\text{mole cm}} \text{ for } 910 \text{ cm}^{-1} \text{ and } 36.7 \frac{1}{\text{mole cm}} \text{ for } 955 \text{ cm}^{-1}$$

$$\text{dibromobutene: } \epsilon_2^0 = 67.5 \frac{1}{\text{mole cm}}$$

TABLE I

a) cOctene: large, constant; cDibromobutene: varying

Absorbance 910 cm ⁻¹			Peak 1-Octene 910 cm ⁻¹	Peak Dibromo- butene	Peak 1-Octene 995 cm ⁻¹	Absorbance 995 cm ⁻¹		
Meth. 1	Meth. 2	Meth. 3				Meth. 1	Meth. 2	Meth. 3
773	763	768	16.8	—	58.1	230	199	215
782	755	769	16.0	53.2	53.9	241	185	214
784	754	769	16.1	35.5	55.0	242	184	214
786	754	770	15.8	22.9	52.4	242	171	208

b) cOctene: varying; cDibromobutene: large, constant

Absorbance 909 cm ⁻¹			Peak Dibromo- butene	Peak 1-Octene 910 cm ⁻¹	Peak 1-Octene 995 cm ⁻¹
Meth. 1	Meth. 2	Meth. 3			
561	561	561	26.3	—	—
574	532	555	25.2	48.8	76.8
584	520	553	24.3	26.7	63.5
598	522	562	22.9	15.8	52.4

c) cOctene: medium, constant; cDibromobutene: varying

Absorbance 910 cm ⁻¹			Peak* 1-Octene 910 cm ⁻¹	Peak* Dibromo- butene	Peak* 1-Octene 995 cm ⁻¹	Absorbance 995 cm ^{-1**}		
Meth. 1	Meth. 2	Meth. 3				Meth. 1	Meth. 2	Meth. 3
298	296	297	44.6	—	74.0	74.8	64.3	69.8
300	293	297	44.3	68.0	73.4	77.3	61.7	69.3
302	292	297	44.1	56.6	72.2	82.5	61.6	72.4
303	291	297	44.0	45.7	71.7	83.5	61.5	72.9

d) cOctene: varying; cDibromobutene: medium, constant

Absorbance 909 cm ⁻¹			Peak* Dibromo- butene	Peak* 1-Octene 910 cm ⁻¹	Peak* 1-Octene 995 cm ⁻¹
Meth. 1	Meth. 2	Meth. 3			
270	270	270	48.0	—	—
279	268	273	46.7	68.6	82.8
283	263	273	45.9	54.3	76.8
282	255	269	45.7	44.0	71.7

e) cOctene: small, constant; cDibromobutene: varying

Absorbance 995 cm ⁻¹			Peak 1-Octene 995 cm ⁻¹	Peak Dibromo- butene
Meth. 1	Meth. 2	Meth. 3		
41.0	34.0	37.5	91.0	—
38.4	29.8	33.9	90.0	78.0
46.3	27.5	37.0	88.8	51.5
50.6	22.7	36.7	87.4	35.4
47.8	22.2	35.4	85.9	25.1

f) cOctene: varying; cDibromobutene: small, constant

Absorbance 909 cm ⁻¹			Peak Dibromo- butene	Peak 1-Octene 910 cm ⁻¹	Peak 1-Octene 995 cm ⁻¹
Meth. 1	Meth. 2	Meth. 3			
52.5	52.5	52.5	88.0	—	—
63.4	51.5	57.3	86.5	73.3	92.0
73.5	51.3	62.7	83.0	39.4	76.7
82.3	51.2	67.0	80.0	24.5	65.0
94.5	42.5	69.3	76.9	14.8	53.9

* The peak values are in per cent transmission.

** The absorbance values are multiplied by 10³.

The two initial solutions had the following concentrations: 1-octene, $c = 0.0961 M$, and dibromobutene, $c = 0.2000 M$.

Mixtures were prepared from these 2 solutions and in order to simplify matters the total concentration, which usually is determined by the iodine monochloride method, was calculated:

Mixture I 1-octene:dibromobutene = 3:2 $c_0 = 0.1376 M$

Mixture II 1-octene:dibromobutene = 3:5 $c_0' = 0.1610 M$

From the 2 mixtures dilution series with 6 samples each were prepared, the operational extinction coefficients were calculated and extrapolated to $c = 0$, whereby the following values were obtained:

	910	995	970
Mixture I	58.0	13.5	39.5
Mixture II	34.0	8.2	52.6

From these 2 values the per cent composition can be calculated by means of procedure 2 which uses the ϵ^0 values as already measured for the pure substances:

		Theory in %	Found in %	Difference in %
Mixture I	1-Octene (910 cm^{-1})	41.9	39.2	-2.7
	1-Octene (995 cm^{-1})	41.9	36.8	-5.1
	Dibromobutene (970 cm^{-1})	58.1	58.5	+0.4
Mixture II	1-Octene (910 cm^{-1})	22.4	23.0	+0.6
	1-Octene (995 cm^{-1})	22.4	22.3	-0.1
	Dibromobutene (970 cm^{-1})	77.6	77.0	-0.6

According to the coupling method (procedure 1) the following results are obtained by means of Equation (6)

	Theory	Found	Difference
ϵ_1^0 (910 cm^{-1})	148.0	133.8	-14.2
ϵ_1^0 (995 cm^{-1})	36.7	30.2	- 6.5
ϵ_2^0 (970 cm^{-1})	67.5	69.7	+ 2.2

Coupling the 2 mixtures gives according to (6) the following values (for a the octene band at 910 cm^{-1} and for b the 995 cm^{-1} band were used):

		a			b		
		Theory in %	Found in %	Diff. in %	Theory in %	Found in %	Diff. in %
Mixture I	1-Octene	41.9	43.4	+1.4	41.9	44.6	+2.7
	Dibromobutene	58.1	56.7	-1.4	58.1	55.4	-2.7
Mixture II	1-Octene	22.4	25.4	+3.0	22.4	27.1	+4.7
	Dibromobutene	77.6	74.6	-3.0	77.6	72.9	-4.7

(The theoretical values were calculated from the ratios of the mixtures.)

For the investigation of a *three-component system* cyclohexene was added as the third component to the 1-octene—dibromobutene mixture. Since this compound shows a band at 910 cm^{-1} , the quantitative determination of the 1-octene had to be done by means of the 995 cm^{-1} band.

The 3 required stock solutions had the following concentrations and extrapolated extinction coefficients:

1-Octene	0.0961 <i>M</i>	36.7 $\frac{1}{\text{Mol. cm}}$
Dibromobutene	0.2000 <i>M</i>	67.5 $\frac{1}{\text{Mol. cm}}$
Cyclohexene	0.3606 <i>M</i>	49.3 $\frac{1}{\text{Mol. cm}}$

Three mixtures were prepared from the 3 stock solutions by a combination of the following amounts (in milliliters):

	1-Octene	Dibromobutene	Cyclohexene
Mixture I	10	15	35
Mixture II	35	10	15
Mixture III	15	30	10

The mole per cent x for the individual components in the mixtures as well as the total concentrations were calculated from these values.

	$c(\text{total})$	$x(\text{octene})$	$x(\text{dibromobutene})$	$x(\text{cyclohexene})$
Mixture I	0.2764	5.8	18.1	76.1
Mixture II	0.1795	31.2	18.6	50.2
Mixture III	0.2009	13.0	54.3	32.6

The following extrapolated extinction coefficients were obtained from the spectra of the 3 prepared dilution series:

	$\epsilon_1(\text{octene})$	$\epsilon_2(\text{dibromobutene})$	$\epsilon_3(\text{cyclohexene})$
Mixture I	2.25	13.7	36.5
Mixture II	10.8	9.1	26.7
Mixture III	4.60	37.0	18.5

The following mole per cent concentrations were obtained according to the evaluation method 2, i.e. Equation (8):

		Theory	Found	Difference
Mixture I	Octene	5.8	6.1	+0.3
	Dibromobutene	18.1	20.3	+2.2
	Cyclohexene	76.1	74.0	-2.1
Mixture II	Octene	31.2	29.4	-1.8
	Dibromobutene	18.6	13.5	-5.1
	Cyclohexene	50.2	54.2	+4.0
Mixture III	Octene	13.0	12.5	-0.5
	Dibromobutene	54.3	54.8	+0.5
	Cyclohexene	32.6	37.5	+3.9

The mathematical coupling of the 3 mixtures yields according to Equation (7) for the actual extinction coefficients the following values:

	Theory	Found	Difference
ϵ_1^0 (995 cm^{-1})	36.7	32.7	4.0
ϵ_2^0 (970 cm^{-1})	67.5	77.6	10.1
ϵ_3^0 (720 cm^{-1})	49.3	48.4	0.9

On the other hand, the compositions of individual mixtures can be determined by means of the ϵ^0 -values according to method I:

		Theory	Found	Difference
Mixture I	Octene	5.8	6.9	+1.1
	Dibromobutene	18.1	17.7	-0.4
	Cyclohexene	76.1	75.4	-0.7
Mixture II	Octene	31.2	33.0	+1.8
	Dibromobutene	18.6	11.7	-6.9
	Cyclohexene	50.2	55.2	+5.0
Mixture III	Octene	13.0	14.1	+1.1
	Dibromobutene	54.3	47.7	-6.6
	Cyclohexene	32.6	38.2	+5.6

Quantitative analysis of polybutadienes.—The course of a polymer analysis is in principle the same as for low molecular weight olefins.

A known quantity of polymer is dissolved in carbon disulfide and the absorption behavior is checked for the strongest band to be used for isomer analysis by recording a partial spectrum. This band should lie in the transmission range of 20–30 per cent. The total concentration of unsaturated components in this stock solution is determined by means of the iodine monochloride method, i.e. the sum of the 1,2, *cis*-1,4 and *trans*-1,4 isomers is determined and expressed in moles of double bonds per liter of solution. The titration is performed conveniently in 1000 ml volumetric flasks, because in such flasks the sample can be shaken easily during the titration. The substance, as well as the iodine monochloride and thiosulfate solutions, is withdrawn from semimicro burets.

An example of the determination of the unsaturation of a styrene-butadiene-copolymer illustrates the procedure. Table II represents the results of 5 parallel determinations which were obtained by titrations and appropriate calculations.

The last places of the buret readings were estimated.

The values in parentheses were discarded. From this stock solution a dilution series with 5–6 samples was prepared, and the concentrations of the diluted samples were again determined with iodine monochloride and expressed in

TABLE II

Run #	1	2	3	4	5	Blank values				
						B1	B2	B3	B4	B5
1. Substance (sample)	0.882	0.860	0.880	0.868	0.892					
2. ICl	3.130	3.080	3.100	3.370	3.150	3.068	3.052	3.030	3.060	3.130
3. ICl = S ₂ O ₃ ²⁻	5.665	5.574	5.611	6.099	5.701	1.8110	1.8093	1.8086	1.8105	(1.8308)
4. S ₂ O ₃ ²⁻	2.200	2.300	2.170	2.710	2.220	5.556	5.522	5.480	5.540	5.730
						Av. 1.8099				
5. Difference	3.465	3.274	3.411	3.389	3.481					
6. $f/2$	0.1741	0.1645	0.1729	0.1703	0.1749					
7. Substance (sample)	0.1974	(0.1913)	0.1965	0.1962	0.1961					

Av. 0.1966M

Line 1: sample polymer solution added, ml. Line 2: iodine monochloride solution added, ml. Line 3: iodine monochloride solution added expressed in ml. of thiosulfate solution used. Line 4: ml of thiosulfate solution consumed for the back titration. Line 5: difference between Lines 3–4. Line 6: Line 5, multiplied by $f/2$. The factor f is the normality of the thiosulfate solution. Line 7: Line 6 is divided by line 1. This furnishes the result in moles of double bonds per liter.

Legend for the blank experiments: Line 2: iodine monochloride solution added, ml. Line 4: ml of thiosulfate solution needed for the titration. Line 3: Line 4 is divided by Line 2. These values indicate how many ml of the thiosulfate solution added are equivalent to 1 ml of the iodine monochloride solution used.

moles of double bonds per liter and they were also calculated with the dilution factor. The infrared spectra of the dilution series were recorded and from these spectra the "operational extinction coefficients" of the individual samples were determined. These ϵ -values are plotted versus concentration (compare Figure 1) and extrapolated to $c = 0$. In this manner a concentration independent operation extinction coefficient is obtained for a certain isomer band. If, for example, a polymer is composed of 1,2, *cis*-1,4 and *trans*-1,4 isomers, then the operational extinction coefficients for the wave numbers 910 cm^{-1} , 680 cm^{-1} and 970 cm^{-1} have to be determined by this method. These 3 coefficients must, in the case of a three-component system, be coupled mathematically with 2 samples of different quantitative composition as described earlier. If, for example, these isomers are to be determined in a polymer which is rich in *trans*-1,4 components, the operational extinction coefficients must be coupled with the extinction coefficients of polymer samples which are rich in

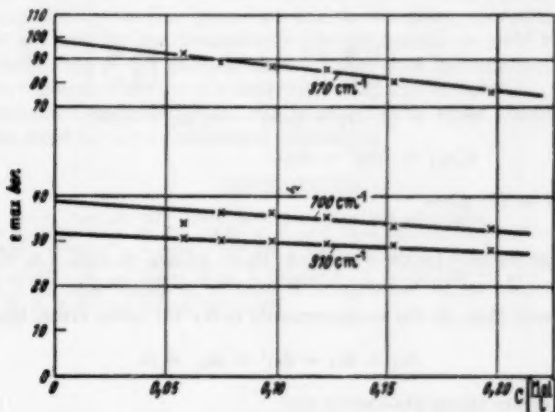


FIG. 1.—Operational extinction coefficients of a polymer composed of 1,2, *cis*-1,4 and *trans*-1,4 isomers.

cis-1,4 and 1,2 isomers (plasticators). Therefore for one analysis 9 operational extinction coefficients are needed. Six of them are obtained by experiments with 2 other polymer samples. However, these values do not have to be determined for each analysis.

In the case of a styrene-butadiene-copolymer the styrene obviously does not interfere with the chemical unsaturation determination. It can be determined separately using specific phenyl group bands. However, the styrene band at 700 cm^{-1} which is most frequently used for the determination of the styrene content interferes with the 680 cm^{-1} *cis*-1,4 band. Therefore it is recommended to determine the *cis*-component for these polymers by difference.

More detailed results of styrene-butadiene-copolymer analyses will be published in another paper.

APPARATUS

The investigations were performed with the aid of a Zeiss Infrared Spectrograph UR 10 having the specifications: Slit program 4, Scanning speed $50\text{ cm}^{-1}/$

min, Writing time 32 sec (time for a full scale deflection), Gain 6, Band width 2, Time constant 2, Recording rate 32 mm/100 cm⁻¹.

DISCUSSION OF THE ERRORS

Let us discuss the errors on the example of a two-component system, because for this case the limits of the usefulness of the new method becomes very clear. For a three-component system the conclusions are analogous although they are harder to recognize.

The total differential for Equation (6c) is as follows:

$$\begin{aligned} d\epsilon_1^0 &= \frac{\partial \epsilon_1^0}{\partial |\epsilon|} d|\epsilon| + \frac{\partial \epsilon_1^0}{\partial |\epsilon_1|} d|\epsilon_1| \\ &= \frac{d|\epsilon|}{|\epsilon_1|} - \frac{|\epsilon|}{(|\epsilon_1|)^2} d|\epsilon_1|; \end{aligned} \quad (9)$$

whereby

$$|\epsilon| = \left| \frac{\epsilon_1 \epsilon_2}{\epsilon_1' \epsilon_2'} \right| \quad \text{and} \quad |\epsilon_1| = \left| \frac{1}{1} \frac{\epsilon_2}{\epsilon_2'} \right| \quad (10)$$

$$d|\epsilon| = (\epsilon_2' d\epsilon_1 + \epsilon_1 d\epsilon_2' - \epsilon_1' d\epsilon_2 - \epsilon_2 d\epsilon_1) \quad (10a)$$

$$d|\epsilon_1| = (d\epsilon_2' - d\epsilon_2). \quad (10b)$$

(10) entered in (9) gives

$$d\epsilon_1^0 = \frac{1}{\epsilon_2' - \epsilon_2} [\epsilon_2' d\epsilon_1 - \epsilon_2 d\epsilon_1' + (\epsilon_1 - \epsilon_1^0) d\epsilon_2' + (\epsilon_1^0 - \epsilon_2') d\epsilon_2]. \quad (11)$$

If it is assumed that all the measurements carry the same error, then

$$d\epsilon_1 = d\epsilon_2 = d\epsilon_1' = d\epsilon_2' = d\epsilon \quad (11a)$$

and all the errors taken absolutely are:

$$d\epsilon_1^0 = \frac{d\epsilon}{\epsilon_2' - \epsilon_2} \cdot (2\epsilon_1^0 + \epsilon_2' + \epsilon_2 - \epsilon_1 - \epsilon_1'). \quad (11b)$$

An analogous equation is obtained for the second coupled component:

$$d\epsilon_2^0 = \frac{d\epsilon}{\epsilon_1' - \epsilon_1} \cdot (2\epsilon_2^0 + \epsilon_1 + \epsilon_1' - \epsilon_2' - \epsilon_2). \quad (11c)$$

The requirement $d\epsilon_1^0 \ll 1$ and $d\epsilon_2^0 \ll 1$ results in addition to the trivial condition $d\epsilon \ll 1$ (i.e. high measuring accuracy) in:

$$a: \epsilon_2' - \epsilon_2 \gg 1 \quad \text{and} \quad \epsilon_1 - \epsilon_1' \gg 1.$$

$$b: (2\epsilon_1^0 + \epsilon_2' + \epsilon_2 - \epsilon_1' - \epsilon_1) = \text{Minimum}$$

$$\text{and: } (2\epsilon_2^0 + \epsilon_1 + \epsilon_1' - \epsilon_2' - \epsilon_2) = \text{Minimum.}$$

Obviously these requirements are best satisfied, if the two mixtures used are as different in composition as possible. Therefore, the calibrations should be performed with highly enriched components. Furthermore, in order to keep

the $d\epsilon$ values as small as possible it is of advantage to repeat the individual measurements several times and to average the measurements. For mixtures of a composition similar to the above example it is better to calculate the percentages by means of already established calibration values (compare 2). Finally, it should be mentioned, that in general with quantitative infrared determinations even under the most favorable circumstances the individual measurements may carry a relative error as high as 4 per cent¹.

SUMMARY

Whereas older methods for the determination of 1,2-, *cis*-1,4 and *trans*-1,4 units in high polymers require pure olefins as calibration substances, this is no longer necessary with the newly developed method which is described in this paper.

From 3 different polymer samples 3 dilution series are prepared and the infrared spectra are recorded. The extinction coefficients are extrapolated to $c = 0$ by a modified base line procedure and the resulting operational extinction coefficients are coupled mathematically (determinants) to yield the actual extinction coefficients of the pure isomers. These may be expressed as mole per cent of the isomeric units for the individual polymer samples.

The procedure described may also be applied to other chemical mixtures without the need for pure calibration substances.

REFERENCES

- ¹ Binder, J. L., *Anal. Chem.* **26**, 1877 (1954); cf. *Z. anal. Chem.* **150**, 123 (1956).
- ² Hampton, R. R., *Anal. Chem.* **21**, 923 (1949); cf. *Z. anal. Chem.* **131**, 124 (1950).
- ³ Hart, E. J. and Meyer, A. V., *J. Amer. Chem. Soc.* **7**, 1980 (1949).
- ⁴ Houben-Weyl, *Methoden der organischen Chemie*, Bd. III/2, G. Thieme Verlag Stuttgart 1955, 8.870.
- ⁵ Lie, T. S., Kolthoff, I. M. and Mairs, M. A., *J. Polymer Sci.* **3**, 66 (1948).
- ⁶ Pirlot, G., *Bull. Soc. chim. Belgique* **55**, 28 (1949); cf. *Z. anal. Chem.* **132**, 361 (1951).
- ⁷ Richardson, W. B., *J. Polymer Sci.* **13**, 229 (1954).

ANIONIC POLYMERIZATION OF ISOPRENE: EFFECT OF IONIC CHARACTER OF THE GROWING ION PAIR ON POLYMER STRUCTURE *

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In a previous publication from this laboratory¹ we noted that the structure of isoprene polymers produced by anionic initiators depended on the ionic character of the growing ion pair ($\text{polymer}^- \text{M}^+$). We also pointed out that the composition of isoprene-styrene copolymers produced by anionic initiators also depended on the ionic character of the growing ion pair¹. The copolymer work was extended in a recent study by Kelley and Tobolsky².

We can now present an extensive correlation between the structure of isoprene homopolymers and the structures of isoprene-styrene copolymers produced under identical conditions of anionic polymerization but with the use of an equimolar mixture of monomers instead of pure isoprene. The polymerizations were carried out at 25° C on 33½ vol-% of monomer (or monomers) in a

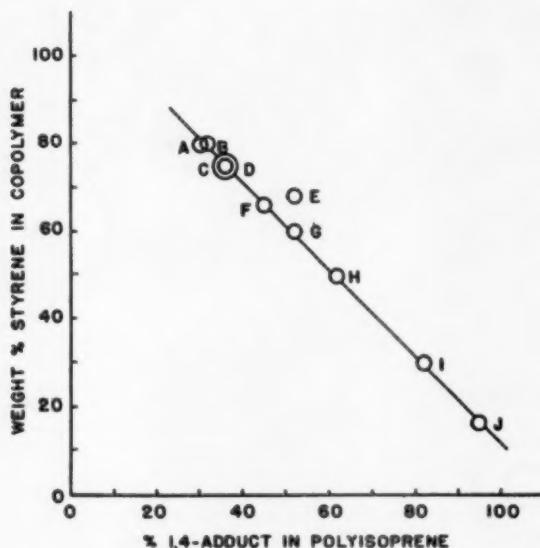


FIG. 1.—Correlation between structure of isoprene homopolymers and composition of styrene-isoprene copolymers.

* Reprinted from the *Journal of Polymer Science*, Vol. 38, pages 205-207 (1959).

TABLE I

Symbol	Initiator	Solvent	Styrene, %	1,4- Adduct, %
A	Li, BuLi	THF	80	30
B	Na	THF	80	32
C	Na	Et ₂ O	75	36
D	BuLi	Me ₂ S	75	36
E	Li, BuLi	Et ₂ O	68	51
F	Na	Hydrocarbons	66	45
G	Li	Et ₃ N	60	52
H	BuLi	Bu ₂ S	50	62
I	BuLi	ϕ_2 O	30	82
J	Li, BuLi	Hydrocarbons	16	95

very wide variety of solvents. The initiators used were butyllithium and metallic dispersions of Li and Na.

Figure 1 shows a plot of per cent 1,4-structure (*cis* + *trans*) in the homopolymer versus weight-per cent of styrene in the initially produced copolymer. The key to this figure and the numerical values are shown in Table I. A linear correlation is obtained between structure of homopolymer and composition of copolymer. The metal counterion (Li^+) and the solvents which would be expected to yield ion pairs of the lowest ionic character produce high 1,4-content of homopolymer and low weight per cent of styrene in the copolymer. On the other end of the scale, the ionic character of the ion pair may be so pronounced that the propagating species may be considered a free anion. There appear to be a definite upper limit of styrene in the copolymer and a lower limit of 1,4-structure in the homopolymer, which may possibly be associated with the propagation of "free" anions.

In Figure 1 it is particularly noteworthy that an almost continuous variation of 1,4-structure was obtained between 95 and 30 per cent. Similarly, an almost continuous variation of weight per cent styrene (between 15 and 80%) was obtained in the copolymers.

From the results of Figure 1 it would certainly appear that the ionic character of the growing ion pair ($\text{polymer}^- \text{M}^+$) is a very important factor in governing the structure of isoprene homopolymers. However, it may not be the only factor.

The ion pairs may be complexed to certain solvents (such as tetrahydrofuran) or to other molecules of initiator, as was found by O'Driscoll and Tobolsky in studies of the kinetics of butyllithium-initiated polymerization of styrene². The exact steric and electrical configurations of such complexes may also affect the disposition of the entering monomers and thus the structure of the final polymer or copolymer. Such effects could be superposed on the general effect of the ionic character of the propagating species which our results show to be of great importance.

SYNOPSIS

The styrene content of styrene-isoprene copolymers initiated by alkali metals in different solvents is correlated with the total 1,4-adduct content of isoprene homopolymers initiated in the same manner. A very good linear relationship is obtained over the whole range which is dependent on the ionic character of the propagating species; highly ionic systems (i.e., Na in ethers) give high styrene and low 1,4-adduct contents, while less ionic systems, i.e., butyllithium

in aromatic ethers and in hydrocarbons, give progressively lower styrene and higher 1,4-adduct contents.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Tobolsky, A. V., Kelley, D. J., O'Driscoll, K. F. and Rogers, C. E., *J. Polymer Sci.* **28**, 425 (1958).
- ² Kelley, D. J. and Tobolsky, A. V., *J. Am. Chem. Soc.* **81**, 1597 (1959).
- ³ O'Driscoll, K. F. and Tobolsky, A. V., *J. Polymer Sci.* **35**, 259 (1959).

ISOPRENE POLYMERIZATION BY ORGANOMETALLIC COMPOUNDS. II *

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INTRODUCTION

The polymerization of isoprene in hydrocarbon media by means of lithium or organolithium initiators produces a polyisoprene comparable to natural rubber containing over 90 per cent of the *cis*-1,4-adduct¹⁻³.

Lithium-dependent initiators are unique in this respect compared with the other alkali metals which produce polyisoprenes containing 1,2-, 3,4-, and *trans*-1,4-adducts. It has been shown⁴⁻⁶ that the polymer structure is controlled by the solvent used as well as by the nature of the positive counterion. For example, with *n*-butyllithium and heptane, over 90% *cis*-1,4-structure was obtained. With *n*-butyllithium and diethylether, the polyisoprene produced contained only 1,2-, 3,4- and *trans*-1,4-adducts; no *cis*-1,4-structure appeared.

In this present work, isoprene was polymerized in a number of solvents by dispersions of metallic lithium, sodium, and potassium, and by some of their organo derivatives. It was our desire to evaluate more fully the influence of solvent and positive counterion on the structure of the polymer. In the past, comparison of results obtained on different polyisoprenes has been hampered by lack of an adequate method of structure analysis. The results of infrared determinations were not always reliable, due to differences in interpretation and calculation. An attempt has been made in this present work to treat the infrared data in a manner which allows more valid comparisons between different polyisoprenes. The values for polyisoprene structure quoted in this paper are tentatively considered to supersede those values for like systems which have been quoted in past publications from this laboratory⁴⁻⁶, wherever there is an appreciable difference.

EXPERIMENTAL

MATERIALS

n-Butyllithium (BuLi) was prepared in benzene or heptane and in diethylether in dry helium atmospheres by the methods of Ziegler⁷ and Gilman⁸, respectively. The resultant solutions were pressure-filtered under dry helium through sintered glass to give clear, colorless solutions. The BuLi concentrations were determined by the double titration method of Gilman⁹. BuLi prepared in benzene or heptane was used in polymerizations carried out in *all* solvents. That prepared in diethylether was used only in polymerizations carried out in diethyl ether, methylal, tetrahydrofuran, and 1,4-dioxane.

Phenylsodium, benzylnsodium, and benzylpotassium were prepared in toluene by the method of Gilman¹⁰.

* Reprinted from the *Journal of Polymer Science*, Vol. 40, pages 73-80 (1959).

The lithium dispersion was supplied by the Lithium Corporation of America and contained 30% lithium by weight, 64% mineral oil, 6% petrolatum, and a small amount of oleic acid as stabilizer. The sodium dispersion was supplied by U. S. Industrial Chemicals Company and contained 35% sodium by weight in white oil No. 52 and was stabilized by 0.5% aluminum stearate. Potassium dispersion was prepared in this laboratory in a mineral oil medium with 1% oleic acid and contained about 25% potassium by weight. No significant differences in structure were found when small pieces of potassium were used in place of the dispersion in hydrocarbon solvents. Small pieces of potassium metal rather than potassium dispersions were used in ether and amine solvents to avoid too violent polymerization in those more active systems.

Phillips polymerization grade isoprene was refluxed over sodium dispersion for two hours and fractionally distilled under dry nitrogen before use. The hydrocarbon, sulfide, and ether solvents were refluxed over sodium wire, the tertiary amines over potassium hydroxide, and distilled under nitrogen or at reduced pressure just prior to use.

POLYMERIZATIONS

The polymerizations initiated by Li dispersion, BuLi, phenyl or benzyl-sodium, or benzylpotassium were conducted in round, 2-oz. bottles fitted with polyethylene gaskets and, usually, magnetic stirrers. Prior to capping, the systems were purged by bubbling through dry helium and/or venting by bringing the monomer to a gentle boil. The polymerizations using sodium or potassium metals were conducted in evacuated sealed tubes.

The concentration of metallic lithium, sodium, or potassium as initiators was approximately 1 mole-% with respect to monomer. BuLi concentrations of 1 to 10 millimoles/mole of monomer were used. The concentration of solvent was 2.5 times that of monomer and at least 100 times that of initiator to insure complete solvation of growing polymer chains. Conversions were in the range of $60 \pm 20\%$. No significant change in structure with conversion was noted within the range of conversion reported.

The polymers were isolated by slowly pouring the reaction mixture into methanol containing phenyl-2-naphthylamine as antioxidant. The product was purified by repeated solution in benzene and precipitation with methanol and was finally dried *in vacuo* at room temperature for one week.

Viscosity measurements of typical samples ranging from sticky semisolids to rubbery solids gave molecular weights of 2000 to 150,000, according to published equations relating intrinsic viscosity and molecular weight¹¹.

ANALYSIS

Infrared spectra of carbon disulfide solutions were obtained on a Perkin-Elmer Model 21 recording spectrophotometer. The relative per cents of the 1,2-, 3,4-, and 1,4-adducts were determined by the method of Richardson and Sacher¹². The ratio of *cis*-1,4- and *trans*-1,4-adducts was estimated by use of a modification of the method of Binder and Ransaw¹³ utilizing the ratio of the corrected absorbances at 8.84 and 8.68 μ , respectively. The composition of each sample calculated from the infrared data was normalized by dividing the concentration of each adduct by the sum of the concentrations of the 1,2-, 3,4-, and 1,4-adducts.

The reproducibility with which the spectrum of any given sample could be recorded and analyzed by the methods used indicates that the sample composition can be reproduced within 5% and the *cis*-to-*trans* ratio within 10% for any given sample and spectrum. This variance in determined composition is probably due to noise level, solvent loss, etc., as they affect the recorded spectrum. The assignment of *cis* or *trans* configuration to the 1,4-adduct of those polyisoprenes containing less than about 70% total 1,4-adduct is considered as only qualitative, due to the experimental difficulties in resolving the spectrum for low 1,4-adduct contents.

A measure of the validity of the determined polymer microstructure is assumed to be given by the correspondence between the magnitude of the total per cent unsaturation found by infrared analysis and the true total unsaturation. The total per cent found by infrared is the sum of the concentrations of the 1,2-, 3,4- and 1,4-adducts found by the infrared method divided by the theoretical total unsaturation from the solids determination, assuming one double bond per monomer residue in the polymer. If all the residual double bonds are involved in the four adducts determined, then the value of the total per cent found should correspond to the true total unsaturation of the polymer which can be estimated by chemical methods; usually the true total unsaturation is about 90 to 95%. Deviations of the true unsaturation from that computed from the infrared spectrum may arise from: (a) mathematical imprecision in determining the absorption coefficients from a given spectrum, (b) errors due to cell mismatch, solvent loss, trace impurities, instrumental errors, and (c) errors inherent in the theoretical basis of the computation, i.e., incorrect extinction coefficients deduced from model compounds, deviations from the Beer-Lambert law, etc.

In order to present the most reliable data possible, only those results are reported herein which gave a value of total per cent found by infrared between the limits of 85% and 105% unsaturation. Further refinement of the limits seems unwarranted because of the errors in determining the absorption values from the recorded spectra. Approximately 15% of our total results yielded exceptionally high or low values of per cent unsaturation and correspondingly wide deviations from the structural pattern obtained in duplicate runs. We do not know whether this is an adventitious instrumental problem or a more fundamental phenomenon; as stated above, we have ignored these occasional discrepancies. The sporadic deviations observed in the analysis may account for the fact that some of the structures reported in earlier papers are different from the "weighted values" obtained here.

It should be mentioned that plots of per cent adduct vs. total per cent found for any given initiator and solvent type gave fairly good linear relationships between the limits 50 to 150 total per cent found. The 1,4-content increased with increase in total per cent found, while the 1,2- and 3,4- contents decreased. By this method of data interpretation it may be possible to qualitatively correlate results within given initiator-solvent systems despite the magnitude of contributing experimental errors. Unfortunately, not enough data are presently available to confirm the validity of this procedure.

We have spent over three years in attempting to work through a completely satisfactory method for determining the microstructure of polyisoprenes by infrared analysis. Our work has been based on the literature in this field and on our various attempts to improve and refine the methods now in use. Nevertheless, we must state that the problem is by no means completely solved.

RESULTS AND DISCUSSION

It has been shown previously^{5,6} that the polymeric structures obtained with lithium dispersion or organolithium compounds are the same when the polymerizations are carried out in bulk or in hydrocarbon solvent; also, they are the same for both types of initiator when the polymerization is carried out in tetrahydrofuran solution, although this structure is quite different from the one above. Likewise, lithium and BuLi in a particular solvent produce copolymers of isoprene-styrene of identical initial styrene content¹⁴. Under otherwise similar conditions, the structures of polyisoprenes produced by lithium-dependent initiators like *n*-butyllithium, amyllithium, phenyllithium, and tolyllithium are not affected by the negatively charged organic fragment of the initiator. Therefore, it has been assumed that polymerizations initiated by alkali metal dispersions proceed via the intermediate formation of metal alkyls (or alkenyls). In the presence of certain solvents an initial reaction may occur between the solvent and the alkali metal. The product then initiates polymerization in the same manner as does any organoalkali metal compound: namely, by addition of the negatively charged organic moiety to a double bond of the monomer.

Regardless of the initiating process, the propagating end of the chain is the ion-pair (\sim isoprene- M^+), where M^+ is the positive alkali metal counterion. It is this ion pair that determines the structure of the resultant polymer, since the entering monomer is strongly influenced by the electrical and steric forces of the ion pair as it insinuates itself between the polymer $^-$ and the M^+ . The nature of this ion pair would be expected to depend on the inherent ionic character of the carbon-alkali metal bond, on the solvating ability of the solvent, and on the dielectric constant of the solvent.

The ion pair may form more or less definite complexes with certain solvents or with other molecules of initiator. The exact steric and electrical configurations of such complexes may also affect the disposition of the entering monomers and thus the structure of the final polymer. Such effects could be superposed on the general effect of the ionic character of the propagating species.

As mentioned above, only those infrared determinations of polyisoprene microstructure which gave per cent found values of total unsaturation between 85 and 105 per cent have been considered as valid. To facilitate the presentation of data, the selected values have been averaged for each individual solvent-initiator system. The resultant average values for polyisoprene microstructure produced in the various solvent-initiator systems at 30° C are listed in Table I along with the number of individual determinations upon which each average is based.

The structures obtained through use either of a particular alkali metal or one of its organoderivatives are essentially identical in any given solvent. However, the method of preparation of phenylsodium, benzylsodium, and benzylpotassium does not exclude the probability that a substantial amount of unreacted alkali metal is also present along with the precipitated organometallic compound. The similarity of polyisoprene structure produced by these organometallic compounds compared with their parent alkali metal may therefore be attributed either to a true similarity like that exhibited by lithium and butyllithium or to a masking polymerization initiated by the metallic "impurities" in the organometallic compound. By analogy with the lithium case and on the basis of the assumed greater reactivity of the organometallic compound over the corresponding metal it is concluded that the former situation is

TABLE I

Solvent	Initiator	Number of determinations	Polyisoprene structure, %				Total* % found
			1,2	3,4	cis-1,4	trans-1,4	
Bulk monomer	BuLi	3	0	8	92	0	95
	Li	2	0	6	94	0	94
	Na	3	7	48	0	45	91
	K	2	8	40	0	52	90
	Rb ^b	—	8	39	5	47	—
	CS ^b	—	8	37	4	51	—
	Alfin (Na) ^b	—	5	16	27	52	—
	Emulsion ^b	—	6	7	22	65	—
<i>n</i> -Heptane	BuLi	3	0	7	93	0	92
	Li	1	0	6	94	0	95
	φNa	2	8	45	0	47	99
	Na	4	10	42	0	48	94
	φCH ₃ K	3	10	38	0	52	100
	K	2	7	35	0	58	99
Cyclohexane	BuLi	1	0	6	94	0	95
	Li	1	0	6	94	0	93
	K	3	7	28	0	65	96
Decalin	BuLi	1	0	6	94	0	99
	K	1	7	34	0	59	98
Benzene	BuLi	5	0	7	93	0	99
	Li	2	0	6	94	0	95
	φNa	1	7	49	0	44	91
	Na	2	9	44	0	47	97
	φCH ₃ K	2	7	41	0	52	95
	K	3	9	39	0	52	98
Toluene	BuLi	2	0	9	91	0	97
	Na	2	7	48	0	45	95
	K	3	9	37	0	54	94
Xylene	BuLi	1	0	8	92	0	87
	Na	1	8	34	0	58	91
	K	2	7	38	0	55	96
Mesitylene	BuLi	1	0	7	93	0	92
	Na	1	9	32	0	59	100
	K	2	9	35	0	56	98
Phenyl ether	BuLi	4	0	18	82	0	92
	Na	1	7	33	0	60	95
	K	3	7	28	0	65	97
Phenyl sulfide	BuLi	4	0	17	83	0	93
	Na	1	8	29	0	63	96
	K	1	8	26	0	66	105
Anisole	BuLi	3	0	34	66	0	94
	Na	1	12	52	0	36	105
	K	2	8	37	0	55	95
<i>N,N</i> -Dimethyl-aniline	BuLi	3	0	35	65	0	92
	Na	1	5	31	0	64	105
	K	2	13	41	0	46	90

* Average value of the number of samples shown.

* Literature values.

TABLE I (Continued)

Solvent	Initiator	Number of determinations	Polyisoprene structure*, %				Total* % found
			1,2	3,4	cis-1,4	trans-1,4	
<i>n</i> -Butyl sulfide	BuLi	4	0	38	62	0	97
	Na	1	12	52	0	36	104
	K	1	8	28	0	64	103
<i>n</i> -Amyl ether	BuLi	2	3	47	0	50	90
	Na	2	12	54	0	34	92
	K	3	11	35	0	54	97
Isopropyl ether	BuLi	1	3	40	0	57	104
	K	1	7	36	0	57	102
Diethyl ether	BuLi	7	4	47	0	49	99
	ϕ Li	2	4	46	0	50	92
	Li	10	5	47	0	48	94
	ϕ Na	3	12	62	0	26	86
	ϕ CH ₂ Na	2	11	52	0	37	94
	Na	5	12	52	0	36	98
	ϕ CH ₂ K	3	10	40	0	50	97
	K	3	12	42	0	46	96
Tri- <i>n</i> -butylamine	Li	1	1	44	0	55	89
	Na	2	8	36	0	56	91
Triethylamine	Li	1	3	45	0	52	101
	K	2	6	24	0	70	98
Methyl sulfide	BuLi	1	6	58	0	36	85
Methylal	BuLi	4	16	54	0	30	94
	Li	3	16	47	0	37	95
	K	2	12	32	0	56	102
Tetrahydrofuran	BuLi	6	16	54	0	30	95
	ϕ Li	1	17	43	0	40	93
	Li	3	14	52	0	34	97
	ϕ Na	3	13	49	0	38	98
	Na	5	15	51	0	34	91
	ϕ CH ₂ K	4	17	40	0	43	98
	K	3	17	35	0	48	102
1,4-Dioxane	BuLi	3	16	49	0	35	93
	Li	6	17	49	0	34	94
	Na	5	9	61	0	30	97
	K	3	14	36	0	50	97

more likely; however, the question must remain in doubt until pure organometallic compounds are used for initiation.

The above problem does not arise in the case of the alkyllithium initiators used, since those compounds are soluble in the media in which prepared and so can be filtered from the unreacted lithium metal.

In Table II, the polymer structures produced by the three different propagating cations have been averaged, where possible, into "solvent classes", the members of each solvent class having essentially identical influence on the polyisoprene structure with the indicated cation.

The solvents in Tables I and II are listed roughly in order of increasing basicity. For lithium-initiated polyisoprenes, as the basicity of the solvent

increases, the relative amounts of 1,2- and 3,4-adducts increase while the 1,4-content decreases. With the exception of those solvents intermediate between "hydrocarbons" and "ethers" listed in Table II, this behavior is characteristic of all three alkali metals and is most apparent from a consideration of the structure ratio of the 1,4-adduct to the sum of the 1,2- and 3,4-adducts. Considering only the general solvent classes in Table II, as we go from "hydrocarbons" to "ethers" to "active ethers" the structure ratio decreases for each of the initiators. Also it may be noted that whereas the ratios for sodium are consistently (0.4 to 0.5) less than those for potassium, the lithium values, both for the magnitudes of the structure ratio and for the stereoisomeric configurations of the 1,4-structure, vary greatly.

The structures of potassium-initiated polyisoprenes vary little with change in type of solvent, attesting to the high inherent ionic character of the potassium-carbon bond. The results of Foster and Binder¹⁸ for the bulk polymerization of isoprene by rubidium and cesium indicate that these more active alkali metals give the same polyisoprene structure as potassium, so that the behavior of potassium may be considered as the "limiting anionic behavior." The change in the structure ratio of sodium-initiated polyisoprenes between the different solvent classes may then be ascribed to the lower inherent ionic character of the sodium-carbon bond which is more sensitive to changes in the solvating or complexing ability of the solvent with subsequent changes in the charge separation of the ion pair. Lithium, with the lowest inherent ionic character of any of the alkali metals, is the most sensitive to changes in solvent environment.

In the more basic ethers and active ethers, lithium acts in a manner approximating the "limiting anionic behavior" and produces polyisoprene of almost the same structure as sodium and potassium. In the less ionizing, nonsolvating hydrocarbons, lithium-dependent initiators produce polyisoprenes with over 90% *cis*-1,4-structure. This dramatic change in polymer structure obtained

TABLE II

Solvent	Solvent class	Propagating cation	Polyisoprene structure, %				Structure ratio [1,4]/ [1,2-3,4]
			1,2	3,4	<i>cis</i> -1,4	<i>trans</i> -1,4	
Bulk monomer, heptane, cyclohexane	"hydrocarbons"	Li	0	7	93	0	13.3
Decalin, benzene, toluene, xylene		Na ^a	9	45	0	46	0.85
Mesitylene		K	9	36	0	55	1.22
Xylene, mesitylene		Na	9	33	0	58	1.38
Phenyl ether		Li	0	18	82	0	4.55
Phenyl sulfide		Na	7	31	0	62	1.63
		K	7	28	0	65	1.86
Anisole, dimethylaniline, <i>n</i> -butyl sulfide		Li	0	36	64	0	1.78
<i>n</i> -Amyl ether	"ethers"	Li	5	46	0	49	0.96
Isopropyl ether		Na	12	55	0	33	0.49
Diethyl ether		K	10	39	0	51	1.04
Methylal	"active ethers"	Li	16	51	0	33	0.49
Tetrahydrofuran		Na	13	54	0	33	0.49
1,4-Dioxane		K	16	36	0	48	0.92

^a Does not include results with xylene and mesitylene.

TABLE III
 (BUTYLLITHIUM AS INITIATOR)

Cosolvent	Volume fraction of heptane	Polyisoprene structure			% found
		1,2	3,4	1,4	
None	1.00	0	7	93	92
Phenyl ether	0.99	0	8	92	95
	0.91	0	9	91	93
	0.73	0	12	88	87
	0.54	0	13	87	87
	0.36	0	14	86	100
	0.17	0	16	84	97
	0.09	0	18	82	92
Phenyl sulfide	0.99	0	8	92	89
	0.98	0	8	92	102
	0.95	0	8	92	96
	0.90	0	11	89	91
	0.70	0	11	89	96
	0.50	0	13	87	94
	0.30	0	15	85	92
	0.10	0	17	83	93
	0.09	0	17	83	93
Anisole	0.99	0	9	91	91
	0.98	0	9	91	94
	0.95	0	11	89	90
	0.90	0	17	83	92
	0.70	0	25	75	96
	0.50	0	31	69	97
	0.30	0	35	65	93
	0.09	0	34	66	94
	0.09	0	34	66	94
Dimethylaniline	0.99	0	9	91	93
	0.98	0	10	90	90
	0.95	0	10	90	88
	0.90	0	15	85	86
	0.70	0	23	77	85
	0.50	0	31	69	85
	0.30	0	34	66	91
	0.10	0	36	64	91
	0.05	0	35	65	92
n-Butyl sulfide	0.99	0	8	92	95
	0.98	0	9	91	87
	0.91	0	13	87	97
	0.73	0	21	79	99
	0.54	0	31	69	97
	0.30	0	37	63	97
	0.17	0	36	64	99
	0.09	0	38	62	103
	0.05	0	38	62	91
n-Amyl ether	0.995	0	12	88	90
	0.985	0	17	83	92
	0.95	0	29	71	100
	0.90	0	42	58	90
	0.80	1	44	55	88
	0.70	1	45	54	95
	0.60	1	49	50	80
	0.50	1	50	49	86
	0.40	1	50	49	85
	0.30	2	48	50	91
	0.10	3	49	48	84
	0.05	3	47	50	90
	0.05	3	47	50	90

TABLE III (Continued)

Cosolvent	Volume fraction of heptane	Polyisoprene structure			% found
		1,2	3,4	1,4	
Ethyl ether	0.995	0	15	85	92
	0.99	0	21	79	95
	0.98	0	33	67	86
	0.95	0	33	67	96
	0.90	0	44	56	88
	0.70	2	44	54	97
	0.50	3	47	50	90
	0.30	4	46	50	96
	0.10	3	52	45	86
	0	4	47	49	99
Tri- <i>n</i> -butylamine	0.995	0	11	89	81
	0.990	0	12	88	81
	0.98	0	14	86	84
	0.95	0	15	85	96
	0.9	0	35	65	84
	0(Li)	1	44	55	89
Triethylamine	0.995	0	20	80	95
	0.990	0	17	83	93
	0.98	0	28	72	86
	0.95	0	36	64	91
	0.9	2	40	58	97
	0.7	3	49	48	88
	0(Li)	3	45	52	101
Methyl sulfide	0.995	0	8	92	99
	0.99	0	10	90	90
	0.98	0	10	90	98
	0.95	0	13	87	89
	0.90	0	21	79	85
	0.70	0	41	59	92
	0.50	2	56	42	88
	0.30	4	58	38	90
	0.10	6	58	36	85

by means of lithium-dependent initiators in hydrocarbon media may well represent the limiting structural form produced by systems with a propagating ion pair of sufficiently low ionic character.

Organic sulfides and aromatic ethers and amines appear to be intermediate between hydrocarbons and aliphatic ethers in solvent behavior. The *cis*-1,4-contents of lithium-initiated polyisoprenes gradually decrease in the intermediate solvents as the solvent becomes more basic; the *cis-trans* ratios in butyl sulfide, anisole, and dimethylaniline are not firmly established, but appear to be probably all *cis*. On the other hand, sodium and potassium in intermediate solvents produce essentially similar polyisoprene structures which have higher *trans*-1,4-contents than are found in either hydrocarbons or ethers. Indeed, sodium in the more basic hydrocarbons xylene and mesitylene produces a polyisoprene structure similar to that produced by potassium and significantly different from the structure produced by sodium in the other hydrocarbons. The intermediate solvating or complexing ability of these solvents is presumably due to (a) the lesser inherent basicity of sulfur compounds compared with the corresponding oxygen compounds, (b) the ability of phenyl groups to act as "electron sinks," thereby reducing the electron density on the sulfur, oxygen, or nitrogen atom, and/or (c) steric hindrance to cation coordination imposed

TABLE IV
TETRAHYDROFURAN AS COSOLVENT

Volume fraction of heptane	[THF]/[BuLi]	Polyisoprene structure, %			% found
		1,2	3,4	1,4	
1.000	0	0	7	93	92
0.999	0.25	1	13	86	101
0.998	0.50	1	20	79	91
0.996	1	1	32	67	103
0.995	—	0	40	60	93
0.992	2	—	—	35	*
0.984	4	—	—	32	*
0.975	—	10	57	33	84
0.968	8	—	—	30	*
0.90	—	12	57	31	86
0.70	—	14	60	26	85
0.30	—	15	55	30	91
0.00	—	16	54	30	95

* Corrected to 95% found by extrapolation.

by the bulky phenyl groups. The gradually decreasing *cis*-1,4-content of the lithium-initiated polyisoprenes may be indicative of either incomplete solvation of the ion-pair by the less basic solvent or else may be a result of a slower attainment of equilibrium solvation of the initially associated alkyllithium compound by these less reactive complexing solvents, or both.

The effect on the resultant polyisoprene structure of changes in the hydrocarbon/cosolvent ratio has been investigated for the system butyllithium-heptane-cosolvent-isoprene at 30° C. The results for several different cosolvents are presented in Tables III and IV. Volume fractions were calculated assuming additive volumes on mixing. The volume of the monomer was con-

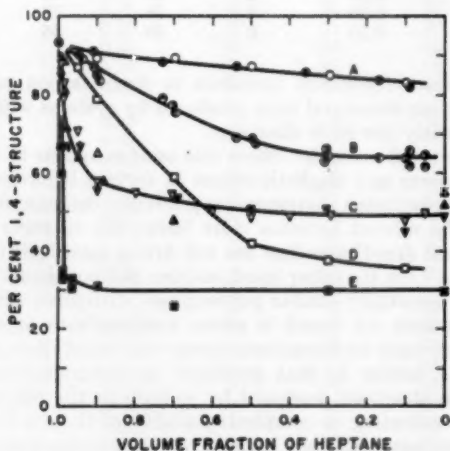


Fig. 1.—Effect of heptane-cosolvent ratio on structure of polyisoprenes initiated by butyllithium. (⊗) n-Heptane. Curve A: (○) phenyl sulfide; (●) phenyl ether. Curve B: (◐) anisole; (◑) N,N-dimethylaniline; (◒) n-butyl sulfide. Curve C: (▽) n-amyl ether; (▼) ethyl ether; (△) tri-n-butylamine; (▲) triethylamine. Curve D: (◻) methyl sulfide. Curve E: (◼) tetrahydrofuran.

stant in each case and was not included in the calculation of solvent volume fractions.

In Figure 1, the total 1,4-content of the resultant polyisoprene has been plotted as a function of heptane volume fraction for the several systems studied. Three general effects may be noted. First, solvents within a given solvent class, as defined in Table II, give identical polyisoprenes at the same volume fractions over the entire range of solvent composition. This tends to confirm, in part at least, the validity of classifying solvents into the various distinct types. Second, the fact that there is often no difference between oxygen, sulfur, and nitrogen compounds of otherwise quite similar structure may indicate that the major effect is of a steric nature. Examples of this behavior are phenyl ether and phenyl sulfide, anisole and dimethylaniline, and the tertiary aliphatic amines and the aliphatic ethers. On the other hand, *n*-butyl

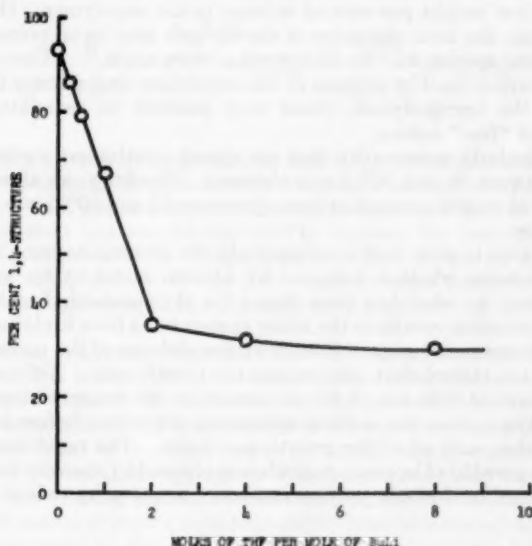


FIG. 2.—Effect of trace tetrahydrofuran on structure of polyisoprenes initiated by butyllithium in hydrocarbons.

sulfide gives the same effect as anisole, while methyl sulfide does not follow any of the other trends. Third, the cosolvent volume fraction at which the structure becomes constant decreases as the solvating power of the cosolvent increases. This would indicate again that a definite complex is formed between the ion-pair and the solvent and that the less hindered the solvent, the more efficiently is the complex formed.

The extreme sensitivity of lithium-dependent initiators to traces of the more active ethers is graphically illustrated in Figure 2 where the total per cent 1,4-structure of the resultant polyisoprene is plotted versus the molar ratio of tetrahydrofuran (THF) to *n*-butyllithium (BuLi)¹⁶. As can be seen, the amount of 1,4-structure decreases with increase in the trace THF content up to the point where two THF molecules are associated with each BuLi molecule.

Ratios of THF to BuLi greater than two give essentially the same polyisoprene structure as when the polymerization is carried out in a gross THF medium.

These results tend to confirm, in part, the kinetic scheme previously proposed by O'Driscoll and Tobolsky¹⁷ for the anionic polymerization of styrene by *n*-butyllithium in benzene-THF solution when the THF/BuLi ratio is less than two.

In a previous publication from this laboratory¹⁸, an extensive correlation was presented between the microstructure of isoprene homopolymers and the initial styrene content of isoprene-styrene copolymers produced under otherwise identical conditions of anionic polymerization with lithium- and sodium-dependent initiators in various solvents. A linear correlation was obtained between the structure of the homopolymer and the composition of the copolymer. The metal counterion (Li) and the solvents which would be expected to yield ion pairs of the lowest ionic character produce high 1,4-content in the homopolymer and low weight per cent of styrene in the copolymer. On the other end of the scale, the ionic character of the ion pair may be so pronounced that the propagating species may be considered a "free anion." There appears to be a definite upper limit of styrene in the copolymer and a lower limit of 1,4-structure in the homopolymer, which may possibly be associated with the propagation of "free" anions.

It is particularly noteworthy that an almost continuous variation of 1,4-structure (between 95 and 30%) was obtained. Similarly, an almost continuous variation of weight per cent styrene (between 15 and 80%) was obtained in the copolymers.

It is desirable to note that copolymers in the styrene-isoprene system give identical structures whether initiated by lithium metal or by butyllithium. This is contrary to what has been found for styrene-methyl methacrylate¹⁹. The copolymerization results in the latter system have been explained as resulting from an electron exchange of lithium atoms with one of the monomers which results in an ion-radical that can propagate at both ends. Lithium may well form an ion-radical with one of the monomers in the isoprene-styrene system. However, in this system the radicals apparently recombine before any appreciable propagation, and all of the growth is anionic. The rapid recombination (compared to growth) of isoprene radicals is evidenced by the very low molecular weights obtained in the bulk polymerization of isoprene by radical initiators²⁰.

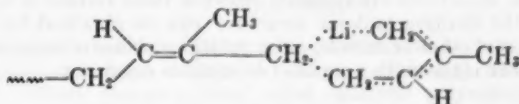
CONCLUSION

From the above results it would certainly appear that the ionic character of the growing ion pair (polymer-M⁺) is a very important factor in governing the structure of isoprene homopolymers.

Another factor which may be sufficient or necessary for the formation of the unique *cis*-1,4-configuration is the presence of an orienting surface or complex. It is well known that organolithium compounds are associated in hydrocarbon media, whereas they are probably monomolecularly dispersed in ethers and amines. It is apparent, then, that in hydrocarbon solutions the carbon-lithium chain end may be associated with other carbon-lithium pairs from unreacted initiator molecules or even with other chain ends or, in some cases, it may be associated with the lithium atoms on the surface of lithium particles. The fact that greater than 90 per cent *cis*-1,4-structure is obtained in hydrocarbons by use of either an apparently clear solution of filtered *n*-butyllithium or a heterogeneous system of lithium dispersion suggests that the massive

surface of the lithium particle is not a *necessary* factor for the stereospecificity of the reaction. Whether we should consider the butyllithium or the lithium-initiated polymerizations as homogeneous solution reactions or heterogeneous surface reactions depends on the definition of a surface, since an associated complex or micelle may also conceivably serve as an orienting specie in the same way as a surface does. We emphasize this since so many stereospecific polymerizations such as the Ziegler system and the Phillips system appear to occur under heterogeneous conditions, presumably on an orienting surface of rather gross dimensions.

The steric requirement for the formation of the *cis*-1,4-adduct therefore can be fulfilled by (a) orientation of the incoming monomer units by association complexes or surfaces, and/or by (b) passing through a transition complex in which all primary and transient bonds are largely covalent, perhaps of a cyclic nature such as^{21,22}:



The addition of a solvent which complexes with the positive counterion, thereby destroying or "poisoning" the association complex or surface, sterically hinders the formation of the complex required for the formation of the *cis*-1,4-adduct. This solvating effect can also be expected to increase the ionic character for solutions of ($\text{---isoprene}^-\text{M}^+$). Regardless of which of the *cis*-1,4-orienting mechanisms is valid, the use of the more basic solvents leads to systems in which neither can operate and so essentially no *cis*-1,4-polymer is produced in these solvents.

To summarize, it appears from the data that the ratio of 1,4- to 1,2- and 3,4-configurations is a function of the ionic character of the propagating ion pair. This ionic character is determined by the inherent ionic nature of the metal-carbon bond and by the basic nature of the solvent as exemplified by its ability to coordinate or complex with the alkali metal counterion. The exact steric and electrical configurations of such complexes may also affect the disposition of the entering monomers and the structure of the final polymer or copolymer. Solvents of strong solvating ability tend to cause all alkali metals to act approximately in the manner of the "limiting anionic behavior" of potassium and so produce^{*} polyisoprenes of similar, though not necessarily identical, microstructure. The appearance of *cis*-1,4-structure in very "covalent" ion-pair propagation has been discussed separately.

SYNOPSIS

Dispersions of metallic lithium, sodium, and potassium and some of their organoderivatives were used to initiate the polymerization of isoprene in several solvents. The propagating species in all cases were ion pairs of the type ($\text{---isoprene}^-\text{M}^+$). The structure of the resultant polyisoprene depends on the character of the propagating ion pair. This in turn depends mainly on the counterion M^+ and the solvent type. One quality of this ion pair which is of utmost importance is its ionic character (or degree of charge separation). In solvents such as diethyl ether and tetrahydrofuran, where we might expect large charge separation in the ion pair, all initiators produce similar, though not

necessarily identical, polymer structures comprising 1,2- 3,4-, and *trans*-1,4-adducts. With potassium-dependent initiators, very nearly the same polymer structure is obtained in hydrocarbons as in the more basic ethers, attesting to the highly ionic character of the potassium-carbon bond; this might perhaps be considered as the "limiting anionic behavior." Sodium has smaller inherent ionic-character and is more sensitive to changes in solvent basicity, but still it parallels the behavior of potassium. With lithium, the most covalent of the alkali metals, a dramatic change in behavior occurs when polymerization is conducted in hydrocarbon media; a 93% *cis*-1,4-, 7% 3,4-polyisoprene structure is obtained. This may be merely a limiting structural form at the low end of the scale of ionic character of the propagating ion-pair. The steric factors arising from complexes formed between the propagating ion-pair and certain solvents or other initiator molecules may also have an important influence on the polymer structures produced in the various solvents. A continuous series of polyisoprene structures intermediate between those formed in hydrocarbons with Li and the limiting 'anionic structure' can be obtained by use of such solvents as phenyl ether or anisole, or by judicious choice of appropriate hydrocarbon-cosolvent ratios with a number of suitable cosolvents.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Staveland, F. W., et al., *Ind. Eng. Chem.* **48**, 778 (1956).
- ² Gibbs, C. F., paper presented to the Division of Polymer Chemistry, 131st Meeting of the American Chemical Society, Miami, April 1957.
- ³ Diem, H. E., Tucker, H. and Gibbs, C. F., paper presented to the Division of Rubber Chemistry, 132nd Meeting, American Chemical Society, New York, September, 1957.
- ⁴ Haieh, H. and Tobolsky, A. V., *J. Polymer Sci.* **25**, 245 (1957).
- ⁵ Haieh, H., Kelley, D. J., and Tobolsky, A. V., *ibid.* **26**, 240 (1957).
- ⁶ Morita, H. and Tobolsky, A. V., *J. Am. Chem. Soc.* **79**, 5853 (1957).
- ⁷ Ziegler, K. and Colonius, H., *Ann.* **479**, 135 (1930).
- ⁸ Gilman, H., Beel, J. A., and Brannen, C. G., *J. Am. Chem. Soc.* **71**, 1499 (1949).
- ⁹ Gilman, H. and Haubein, A. H., *J. Am. Chem. Soc.* **66**, 1515 (1944).
- ¹⁰ Gilman, H., Pacevits, H. A., and Baine, O., *J. Am. Chem. Soc.* **62**, 1514 (1940).
- ¹¹ Carter, W. C., Scott, R. L., and Magat, M., *J. Am. Chem. Soc.* **68**, 1840 (1946).
- ¹² Richardson, A. and Sacher, W., *J. Polymer Sci.* **14**, 353 (1953).
- ¹³ Binder, J. L. and Ransaw, H. C., *Anal. Chem.* **29**, 503 (1957).
- ¹⁴ Kelley, D. J. and Tobolsky, A. V., *J. Am. Chem. Soc.* **81**, 1597 (1959).
- ¹⁵ Foster, F. C. and Binder, J. L., in *Handling and Use of the Alkali Metals*, *Advances in Chemistry No. 19*, American Chemical Society, Washington, 1957, p. 27.
- ¹⁶ Whitesacre, H. M., Senior Thesis, Princeton University, 1958.
- ¹⁷ O'Driscoll, K. F. and Tobolsky, A. V., *J. Polymer Sci.* **35**, 259 (1959).
- ¹⁸ Tobolsky, A. V. and Rogers, C. E., *J. Polymer Sci.* **38**, 205 (1959).
- ¹⁹ O'Driscoll, K. F., Boudreau, R. J., and Tobolsky, A. V., *J. Polymer Sci.* **31**, 115, 123 (1958); **37**, 363 (1959).
- ²⁰ Conwell, Y., Roesser, G. P., and Tobolsky, A. V., *J. Polymer Sci.* **4**, 309 (1949).
- ²¹ Overberger, C. G., Private communication.
- ²² Stearns, R. S. and Forman, L. E., paper presented to the Division of Rubber Chemistry, 134th Meeting, American Chemical Society, Chicago, September 1958, *J. Polymer Sci.* **41**, 381 (1959); see also this issue, p. 595.

MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS. POLYMERIZATION OF ISOPRENE AND BUTADIENE WITH METAL ORGANIC COMPOUNDS

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INTRODUCTION

Recently there has been intensive study as well as industrial application of polymerization processes initiated by alkali metals and metal organic compounds¹⁻⁷. These processes, here called catalytic polymerization, are quite different from the longer known processes of radical polymerization. They are characterized by the formation of intermediate complexes which not only initiate the polymerization but which also influence the structure of each unit of the polymer chain. It should be noted that in radical polymerization the macromolecules attain their final length in hundredths or thousandths of a second, while the growth of each macromolecule can last minutes and even hours in catalytic polymerization.

For the study of mechanism of catalytic polymerization there is considerable interest in the analysis of the distribution of polymer molecules with respect to degree of conversion (or molecular weight) which will permit, through comparison of theoretical and experimental molecular weight distributions (MWD), the detection of the presence of partial (intermediate) reactions and the determination of their role in the complete polymerization process.

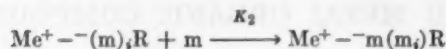
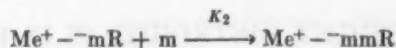
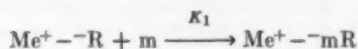
The present paper examines the problems associated with the calculation and analysis of the theoretical molecular weight distributions and considers, on the basis of this analysis, experimental data from a study of samples of polybutadiene and polyisoprene obtained by polymerization in solution with butyllithium. The selection of butyllithium as catalyst was based on its known solubility in saturated hydrocarbons, which tends to give the polymerization a homogeneous character and considerably simplifies the analysis of the results.

1. THE THEORY OF MOLECULAR-WEIGHT DISTRIBUTIONS IN CATALYTIC POLYMERIZATION

In the case of metal organic catalysts the attachment of the first monomer unit occurs on the strongly polarized bond of the metal⁺-hydrocarbon radical. The subsequent molecules of monomer are inserted between the metal

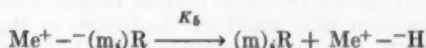
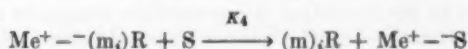
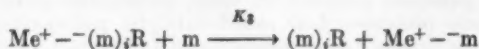
* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY, from *Zhur. Tekh. Fiz.* 28, 114-131 (1958).

and the growing chain:



etc.; where Me is the metal, R the hydrocarbon radical, m the monomer, K_1 and K_2 the rate constants of the initiation and growth of the chain, respectively. In the general case, $K_1 \neq K_2$. The main causes of termination in the growth of the chain are transfer reactions of active site to the monomer or solvent and also the first order degradation of the active site with release of the catalyst.

These reactions occur as follows⁸:



where K_3 , K_4 and K_5 are the rate constants of transfer to monomer, the transfer to the solvent S, and of the unimolecular release of the catalyst in the form of a metal hydride.

During initiation of the polymerization reaction by alkali metals an active site presumably arises through reaction of the metal with monomer or solvent to form a metal organic compound, after which chain growth takes place according to the above equations⁸.

A somewhat different treatment of the process is also possible^{5,8,9} in which the active site is considered to be a complex consisting of the initial metal organic compounds and of the added molecules of the monomer and solvent, the latter acting as cocatalysts. In this case the constant K_1 characterizes the rate of formation of the catalytic complex.

Theoretical calculation and analysis of the MWD for catalytic polymerization can be made according to either of two methods. Taking into account the inherent discontinuity of polymerization, wherein the individual monomer units are added one at a time to growing chain, we can set up a series of differential equations which can be readily solved. However, the solution obtained is in the form of a rather complex series. It is possible to make a simplification at the outset. If the polymerization is approximately represented as the uninterrupted growth of a chain, the problem is more easily solved, but some details are lost during such a treatment. We shall show here both methods for calculating MWD.

(a) *Calculation of MWD taking into account the discontinuous nature of polymerization.*—A series of rate equations follows starting with the assumption that chain growth is restricted by transfer of the active site to monomer. To avoid introducing a supplementary parameter, which could make subsequent

calculations cumbersome, we shall consider the catalyst which is formed as a result of the transfer reaction to be equal in activity to the original one¹.

$$\left. \begin{aligned} dc/dt &= -K_1cm + K_3m \sum_i A_i \\ dA_1/dt &= K_1cm - K_2A_1m - K_3A_1m \\ dA_2/dt &= K_2A_1m - K_2A_2m - K_3A_2m \\ dA_3/dt &= K_2A_2m - K_2A_3m - K_3A_3m \\ &\dots \dots \dots \\ dA_i/dt &= K_2A_{i-1}m - K_2A_im - K_3A_im \end{aligned} \right\} \quad (1)$$

where c is the concentration (mole/liter) of the catalyst; $A_1, A_2, A_3 \dots A_i$ are the concentrations (mole/liter) of active sites with the number of structural units 1, 2, 3, $\dots i$; m is the concentration (mole/liter) of monomer units; and t is time (minutes).

The rate of conversion of monomer in the course of the polymerization is described with sufficient accuracy by the following equation:

$$dm/dt = -K_1cm - K_2m \sum_i A_i - K_3m \sum_i A_i$$

We shall introduce a new variable τ and assume that $d\tau = mdt$. Then $\tau = \int_0^t mdt$ may be designated as the relative time¹⁰⁻¹². At any stage in the polymerization τ may be determined analytically (see below) as well as by means of experimentally obtained rate curves¹². K_2 may be determined from the tangent of the graph $\frac{m_0 - m}{m_0} = f(\tau)$. Note that $t = 0$ when $\tau = 0$.

Dividing the above equations by m , we obtain the following series of first order differential equations

$$\left. \begin{aligned} dc/d\tau &= -K_1c + K_3 \sum_i A_i \\ dA_1/d\tau &= K_1c - K_2A_1 - K_3A_1 \\ dA_2/d\tau &= K_2A_1 - K_2A_2 - K_3A_2 \\ dA_3/d\tau &= K_2A_2 - K_2A_3 - K_3A_3 \\ &\dots \dots \dots \\ dA_i/d\tau &= K_2A_{i-1} - K_2A_i - K_3A_i \end{aligned} \right\} \quad (1a)$$

$$dm/d\tau = -K_1c - K_2 \sum_i A_i - K_3 \sum_i A_i \quad (2)$$

Considering that $\sum_i A_i = c_0 - c$, where c_0 is the initial concentration of catalyst (when $\tau = 0$) and also that $A_1, A_2, A_3 \dots A_i = 0$ at $\tau = 0$, and solving Equations (1a) consecutively, we obtain

$$c = \frac{c_0}{K_1 + K_3} (K_1 e^{-(K_1 + K_3)\tau} + K_3) \quad (3)$$

$$A_i = \frac{K_1 K_2^{i-1}}{K_1 + K_3} c_0 e^{-(K_2 + K_3)\tau} \sum_{r=1}^{\infty} [K_1(K_2 - K_1)^{r-i} + K_3(K_2 + K_3)^{r-i}] \frac{\tau^r}{r!} \quad (4)$$

It can also be shown that

$$A_i = \frac{K_1 K_2^{i-1}}{K_1 + K_3} c_0 \left\{ \frac{K_3}{(K_2 + K_3)^i} J[i, (K_2 + K_3)\tau] + \frac{K_1}{(K_1 + K_2)^i} e^{-(K_1 + K_2)\tau} J[i, (K_2 - K_1)\tau] \right\} \quad (4a)$$

where the functions of J are incomplete ($\Gamma[i, \alpha\tau]$) and complete ($\Gamma[i]$) gamma functions, equal, respectively, to $\int_0^{\alpha\tau} e^{-\alpha\tau} (\alpha\tau)^{i-1} d(\alpha\tau)$ and $(i-1)!$. The values of J can be found in tables¹³.

Solving Equation (2), we obtain

$$\delta = \frac{m_0 - m}{m_0} = \frac{c_0}{m_0} \left\{ \frac{K_2 + K_3 - K_1}{K_1 + K_3} \left[e^{-(K_1 + K_3)\tau} \left(1 - \frac{K_3}{K_1 + K_3} \right) - 1 - K_3 \left(\tau - \frac{1}{K_1 + K_3} \right) \right] + (K_2 + K_3)\tau \right\} \quad (5)$$

Since the second term in the right hand side of Equation (2) is the quantitatively important term, we can obtain the simpler expression

$$\delta \simeq \frac{K_1 K_2 c_0}{(K_1 + K_3)^2 m_0} [(K_1 + K_3)\tau + e^{-(K_1 + K_3)\tau} - 1] \quad (5a)$$

By Equations (5) or (5a) we can determine τ for any degree of conversion (δ) for given values of the constants K_1 , K_2 and K_3 , so that Equation (4) permits calculation of MWD for active chains at any stage of polymerization.

For the case when $K_3 = 0$, we obtain

$$A_i = \frac{K_1}{K_2} \left(\frac{K_2}{K_2 - K_1} \right)^i c_0 e^{-K_2\tau} \sum_{r=1}^{\infty} \frac{[(K_2 - K_1)\tau]^r}{r!} \quad (6)$$

or

$$A_i = \frac{K_1}{K_2} \left(\frac{K_2}{K_2 - K_1} \right)^i c_0 e^{-K_1\tau} J[i, (K_2 - K_1)\tau] \quad (6a)$$

$$\delta = \frac{K_2 c_0}{m_0} \left[\tau + \left(\frac{1}{K_2} - \frac{1}{K_1} \right) (1 - e^{-K_1\tau}) \right] \quad (7)$$

Equations (6) and (6a) appear to characterize the distribution of polymer isolated at an appropriate stage of polymerization in the absence of reactions which cause limitation of chain growth.

The average degree of polymerization (\bar{i}) is determined in a given case by the basic equation

$$\bar{i} = \frac{m_0 - m}{\sum_i A_i} = \frac{m_0 \delta}{c_0 - c} \quad (8)$$

The weight MWD, calculated from Equations (6) and (7) are given in Figure 1 (curves 1 and 2). Here (as well as below) the weight fractions

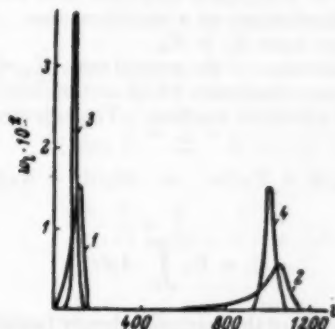


FIG. 1.—1 and 2— $K_1/K_2=0.01$, $K_1=0$, $c_0/m_0=0.001$, $\delta=0.1$ and 1 respectively; 3 and 4— $K_1=K_2=1$, $K_2=0$, $c_0/m_0=0.001$, $\delta=0.1$ and 1 respectively.

$w_i = \frac{iA_i}{m_0 - m}$ are plotted on the ordinate. Characteristic of these distributions is the gentle slope or "tail" on the side of low degree of polymerization which is longer the smaller is K_1 relative to K_2 . When $K_1 = K_2 = K$, then by Equations (6) and (7)

$$A_i = c_0 e^{-K\tau} \frac{(K\tau)^i}{i!} \quad (9)$$

$$\delta = \frac{c_0 K}{m_0} \tau \quad (10)$$

For \bar{i} we obtain

$$\bar{i} = \frac{m_0 \delta}{c_0} = K\tau \quad (11)$$

Substituting in Equation 9, we obtain

$$A_i = c_0 e^{-\bar{i}} \frac{(\bar{i})^i}{i!} \quad (9a)$$

When $i \gg 1$ Equation 9a can be converted into the form of an ordinary Gaussian distribution with standard deviation of $\sqrt{\bar{i}}$

$$A_i = \frac{c_0}{\sqrt{2\pi\bar{i}}} e^{-\frac{(i-\bar{i})^2}{2\bar{i}}} \quad (9b)$$

Physically the case $K_1 = K_2$ corresponds to the case in which the catalyst is introduced into the system already in the final active state and the rate of attachment of the first monomer unit does not much differ from the rate of attachment of subsequent units. MWD calculated by Equations (9) and (10) are shown in Figure 1 (curves 3 and 4). Their relatively low polydispersity and their Gaussian character are caused by the fact that initiation and growth of all chains occurs almost simultaneously and continues until all the monomer reacts, as a result of which the dispersion of the chain lengths is purely statistical. This occurs because an i -mer is formed by i discrete acts of monomer addition. The manner of calculation employed here automatically considers the molecular weight distribution as a statistical one. Similar distributions will probably be obtained when $K_1 > K_2$.

Returning to a consideration of the general case ($K_3 \neq 0$) we shall calculate the MWD for inactive macromolecules which accumulate in the course of polymerization as a result of a transfer reaction. The following is probably the initial rate equation

$$dQ_i/dt = K_3 A_i m \quad \text{or} \quad dQ_i/d\tau = K_3 A_i$$

from which follows

$$Q_i = K_3 \int_0^\tau A_i d\tau \quad (12)$$

Here Q_i is the concentration of the inactive polymer (mole/liter). Substituting the value of A_i from Equation (4) into (12) and integrating, we obtain as a result

$$Q_i = \frac{K_1 K_2^{i-1} K_3 c_0}{(K_1 + K_3)(K_2 + K_3)} e^{-(K_2 + K_3)\tau} \sum_{r=1}^{\infty} \sum_{l=r+1}^{\infty} (K_2 + K_3)^{l-i} \times \left[K_1 \left(\frac{K_2 - K_1}{K_2 + K_3} \right)^{r-i} + K_3 \right] \frac{\tau^l}{l!} \quad (13)$$

The total concentration of i -mers (N_i) in the system is obtained, obviously, from the sum of Equations (4) and (13)

$$N_i = \frac{K_1 K_2^{i-1} c_0}{K_1 + K_3} e^{-(K_2 + K_3)\tau} \left\{ \sum_{r=1}^{\infty} \left[K_1 (K_2 - K_1)^{r-i} + K_3 (K_2 + K_3)^{r-i} \right] \frac{\tau^r}{r!} \right. \\ \left. + \frac{K_3}{K_2 + K_3} \sum_{r=1}^{\infty} \sum_{l=r+1}^{\infty} (K_2 + K_3)^{l-i} \left[K_1 \left(\frac{K_2 - K_1}{K_2 + K_3} \right)^{r-i} + K_3 \right] \frac{\tau^l}{l!} \right\} \quad (14)$$

It is of interest to point out how the presence of transfer reactions affects the MWD. In order to do this let us assume that $K_1 = K_2$ in (14). The distributions will be very narrow and practically symmetrical as was established above for the case when $K_3 = 0$. To simplify the calculations we shall assume also that $K_2 + K_3 = 1$. This assumption is permissible since the expression for the nature of the distribution curve which is to be determined does not contain the absolute values of the constants but rather the relation between them.

Transforming (14) we obtain,

$$N_i = K_2^i c_0 e^{-\tau} \left(\frac{\tau^i}{i!} + 2K_3 \sum_{r=i+1}^{\infty} \frac{\tau^r}{r!} + K_3^2 \sum_{r=i}^{\infty} \sum_{l=r+2}^{\infty} \frac{\tau^l}{l!} \right)$$

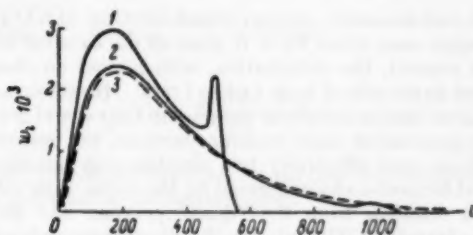


FIG. 2.—1— $\tau=500$; 2— $\tau=1000$; 3— $\tau=2000$, $K_1=K_2=0.995$; $K_3=0.005$.

It can be shown that

$$\sum_{r=i}^{\infty} \sum_{l=r+2}^{\infty} \frac{\tau^l}{l!} = \sum_{n=0}^{\infty} n \frac{\tau^{i+n+1}}{(i+n+1)!}$$

Since,

$$\sum_{r=i+1}^{\infty} \frac{\tau^r}{r!} = \sum_{n=0}^{\infty} \frac{\tau^{i+n+1}}{(i+n+1)!}$$

we have finally

$$N_i = K_2^i c_0 e^{-\tau} \left[\frac{\tau^i}{i!} + K_3 \sum_{n=0}^{\infty} \frac{\tau^{i+n+1}}{(i+n+1)!} (2 + K_3 n) \right] \quad (15)$$

Correspondingly, when $K_3 \ll 1$, Equation (5a) yields

$$\delta \simeq \frac{c_0}{m_0} \tau \quad (16)$$

Let us now analyze the distributions calculated in Equations (15) and (16) (see Figures 2 and 3). First let us note that when the relations between the rate constants are determined. The nature of the distribution depends only on the value of the product $\delta \frac{m_0}{c_0}$ as follows from the general Equations (5) and (14). This means that, by varying the relation between the initial concentra-

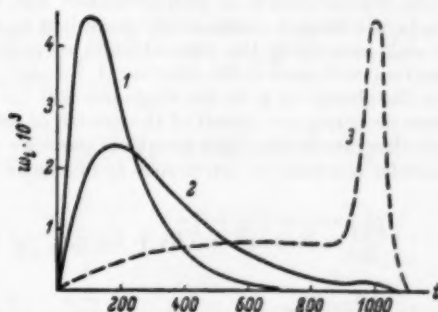


FIG. 3.—1— $K_1=K_2=0.99$, $K_3=0.01$, $\tau=1000$; 2— $K_1=K_2=0.995$, $K_3=0.001$, $\tau=1000$.

tions of catalyst and monomer, one can obtain identical MWD at various values of δ . For a simpler case, when $K_3 = 0$, after all the catalyst initially added to the system has reacted, the distribution, with almost no changes in general form, is displaced to the side of large i when $i \simeq \delta$. However, a slight widening with time may arise from a statistical variance in the rates of growth of separate chains. In the presence of chain transfer reactions, the process becomes more complicated: there exist effectively two simultaneous distributions—the primary one caused by active chains formed by the initial catalyst, and a secondary distribution resulting from the “dead” polymer and the active chains produced by the transfer. The primary distribution corresponds to that given by Equation (6) or, if $K_1 = K_2$ by Equation (9), the only difference being that the primary distribution contribution to the total MWD decreases during the course of the reaction; it behaves as if it diminished with the extent of the shift to the right and does so more rapidly the larger the ratio K_3/K_2 . Finally, a stage could be attained at which the primary MWD has completely disappeared. In stages beyond these the MWD would effectively lose its dependence on δ . In fact, it would now consist entirely of a fully completed secondary distribution for which the condition of a steady state is automatically fulfilled: equality of the rates of limitation and initiation. Figure 2 represents the MWD calculated from Equation (15) and (16) at $K_3/K_2 = 0.005$ and $\tau = 500, 1000$, and 2000 , which at $c_0/m_0 = 1/2000$ corresponds to $\delta = 0.25, 0.5$, and 1 . At $\delta = 0.5$ (curve 2) the primary MWD has practically disappeared and the further course of polymerization has almost no influence on the nature of the distribution. We note that if we had proceeded in our calculations with the value $c_0/m_0 = 1/500$ the steady state would not yet be reached at the time when the polymerization is completed ($\tau = 500$) and the MWD would correspond to curve 1 on Figure 2. The MWD represented in Figure 3 has been calculated with a number of values of the parameters and serves to illustrate that which has been explained above. As follows from Figures 2 and 3, the secondary MWD, in contrast to the primary MWD, is characterized by considerable polydispersity which increases as the ratio K_3/K_2 decreases.

(b) *Approximate calculation of MWD with the assumption of an uninterrupted process of chain growth.*—The calculation of the MWD by the equations selected above is quite cumbersome, particularly in those cases in which it is necessary to include all three rate constants. It is therefore desirable to have expressions which permit quick and simple calculation of the distributions at any values of the parameters even at the sacrifice of some detail. With this in mind we shall assume the discrete representation of polymerization but shall assume the polymer chains to be distributed continuously according to some distribution $\varphi = \varphi(i, t)$, with $\varphi_i \Delta i$ describing the concentration of molecules having degrees of polymerization contained in the interval $(i, i + \Delta i)$.

Let us consider the change in φ_i in the single interval ($\Delta i = 1$) taking into account the increase occurring as a result of the growth of particles containing $i - 1$ units and the decrease arising from growth of particles containing i units as well as from transfer reactions of active sites to monomer.

Then,

$$\frac{\partial \varphi_i}{\partial t} = K_2 \varphi_{i-1} m - (K_2 + K_3) \varphi_i m$$

or

$$\frac{\partial \varphi_i}{\partial \tau} = K_2 \varphi_{i-1} - (K_2 + K_3) \varphi_i \quad (17)$$

Considering that $\varphi_{i-1} = \varphi_i - \frac{\partial \varphi_i}{\partial i}$, we obtain

$$\frac{\partial \varphi_i}{\partial \tau} = -K_2 \frac{\partial \varphi_i}{\partial i} - K_3 \varphi_i \quad (18)$$

This is the basic differential equation for the distribution function φ . The following equation is the limiting case:

$$\frac{\partial \varphi_1}{\partial \tau} = K_1 c - (K_2 + K_3) \varphi_1 \quad (19)$$

Assume the initial condition to be: at $\tau = 0$, $\varphi_i = 0$ ($i = 1, 2, 3, \dots \infty$).

Using the Laplace transformation $\bar{\varphi} = \int_0^\infty \varphi e^{-p\tau} d\tau$, where $\bar{\varphi}$ is the transform of the function φ and p is a parameter, and the usual rule concerning the transform of a derivative, and also taking into account Equation (3), we obtain in transform equations analogous to (18) and (19).

$$p \bar{\varphi}_i = -K_2 \frac{\partial \bar{\varphi}_i}{\partial i} - K_3 \bar{\varphi}_i \quad (20)$$

$$p \bar{\varphi}_1 = \frac{K_1 c_0}{K_1 + K_3} \left(\frac{K_1}{K_1 + K_3 + p} + \frac{K_3}{p} \right) - (K_2 + K_3) \bar{\varphi}_1 \quad (21)$$

Solving Equation (20) by introducing the limiting conditions (21), we obtain

$$\bar{\varphi}_i = \frac{K_1 c_0}{(K_1 + K_3)(K_2 + K_3 + p)} \left[\frac{K_1}{(K_1 + K_3 + p)} + \frac{K_3}{p} \right] e^{-\frac{K_3 + p}{K_2}(i-1)} \quad (22)$$

It now remains to convert the transform $\bar{\varphi}_i$ to the desired function φ_i by means of the inversion relation according to which

$$\varphi_i = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \bar{\varphi}_i e^{p\tau} dp.$$

Replacing the integration along the contour with line integration and taking into account the points $p = 0$, $-(K_1 + K_3)$ and $-(K_2 + K_3)$, which are simple poles, we obtain

$$\begin{aligned} \varphi_i = \frac{K_1 c_0 e^{-\frac{(i-1)K_3}{K_2}}}{K_1 + K_3} & \left[\frac{K_1}{K_2 - K_1} \left(e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_2 + K_3)} \right) \right. \\ & \left. + \frac{K_3}{K_2 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_2 + K_3)} \right) \right] \beta \left(\tau - \frac{i-1}{K_2} \right) \quad (23) \end{aligned}$$

The function $\beta \left(\tau - \frac{i-1}{K_2} \right)$ can take only two forms: at $\tau < \frac{i-1}{K_2}$, $\beta = 0$

and at $\tau > \frac{i-1}{K_2}$, $\beta = 1$. In the discussion following it will not be written in explicit form.

Equation (23) is analogous to Equation (4). Assuming that $K_3 = 0$ we obtain

$$\varphi_i = \frac{K_1 c_0}{K_2 - K_1} \left(e^{-\left(\tau - \frac{i-1}{K_1}\right) K_1} - e^{-\left(\tau - \frac{i-1}{K_2}\right) K_2} \right) \quad (24)$$

or at $K_1 \ll K_2$

$$\varphi_i = \frac{K_1 c_0}{K_2} e^{-\left(\tau - \frac{i-1}{K_1}\right) K_1} \quad (25)$$

Figure 4 shows the MWD calculated with equal parameters ($K_1 = 0.001$; $K_2 = 1$; $\tau = 2000$) according to Equation (6) (curve 2) and Equation (25) (curve 1). The steep drop of curve 1 on the side of larger i is explained by the

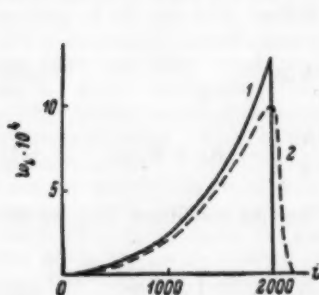


Fig. 4.— $K_1 = 0.001$, $K_2 = 1$, $\tau = 2000$.
1—Calculation according to Equation (25);
2—Calculation according to Equation (6).

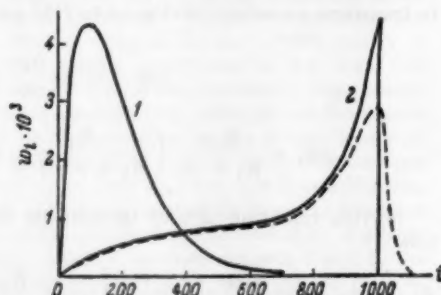


Fig. 5.—1— $K_1 = 0.001$, $K_2 = 1$, $K_3 = 0.01$, $\tau = 1000$;
2— $K_1 = 0.01$, $K_2 = 1$, $K_3 = 0.001$, $\tau = 1000$. Dotted line
is correction of curve 2 considering distribution of growth
rates of individual chains.

fact that the method described, in contrast to the former method, does not take into account the discontinuous nature of the polymerization process and thus neglects the statistical dispersion in the growth rates of individual chains.

Setting $K_1 = K_2 = K$ in Equation (24) and removing the resulting indeterminacy, we obtain

$$\varphi_i = K c_0 \left(\tau - \frac{i-1}{K} \right) e^{-\left(\tau - \frac{i-1}{K}\right) K} \quad (26)$$

The MWD calculated from Equation (26) is practically completely monodisperse.

Proceeding in a manner analogous to the above we shall calculate the integral $\psi_i = \int_{\frac{i-1}{K_1}}^{\tau} \varphi_i d\tau$, where ψ_i is the distribution function for the "dead"

polymer and φ_i is given by Equation (23).

$$\psi_i = \frac{K_1 K_3 c_0}{K_1 + K_3} e^{-\frac{(i-1)K_1}{K_1}} \left\{ \frac{K_1}{K_2 - K_1} \left[\frac{1}{K_1 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \right. \right. \\ \left. \left. - \frac{1}{K_2 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \right] + \frac{K_3}{K_2 + K_3} \left[\left(\tau - \frac{i-1}{K_2} \right) \right. \right. \\ \left. \left. - \frac{1}{K_2 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \right] \right\} \quad (27)$$

The complete distribution is evidently given by the following expression:

$$\chi_i = \varphi_i + \psi_i = \frac{K_1 c_0 e^{-\frac{(i-1)K_1}{K_1}}}{K_1 + K_3} \left\{ \frac{K_1}{K_2 - K_1} \left[e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right. \right. \\ \left. \left. - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} + \frac{K_3}{K_1 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \right] \right. \\ \left. + \frac{K_3}{K_2 + K_3} \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \times \left(1 - \frac{K_3}{K_2 + K_3} \right. \right. \\ \left. \left. - \frac{K_1}{K_2 - K_1} \right) + \frac{K_3^2}{K_2 + K_3} \left(\tau - \frac{i-1}{K_2} \right) \right\} \quad (28)$$

If K_1 and K_3 are considerably smaller than K_2

$$\chi_i \simeq \frac{K_1 c_0 e^{-\frac{(i-1)K_1}{K_1}}}{K_2 + K_3} \left\{ \frac{K_1}{K_2 - K_1} \left[e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} + \frac{K_3}{K_1 - K_3} \right. \right. \\ \left. \left. \times \left(1 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) \right] + \frac{K_3}{K_2 + K_3} \left[K_3 \left(\tau - \frac{i-1}{K_2} \right) + 1 \right] \right\} \quad (29)$$

In many actual cases, the last equation can in turn be simplified. The distributions calculated from Equation (29) are given in Figure 5.

Assuming $K_1 = K_3$ in (28) and removing the indeterminacy, we obtain

$$\chi_i = \frac{K_2 c_0}{K_2 + K_3} e^{-\frac{(i-1)K_3}{K_2}} \left\{ K_3 \left(\tau - \frac{i-1}{K_2} \right) e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right. \\ \left. - \frac{K_3}{K_2 + K_3} \left[K_3 \left(\tau - \frac{i-1}{K_2} \right) + \frac{1}{K_2 + K_3} e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right. \right. \\ \left. \left. - \frac{K_2}{K_2 + K_3} \left(2 - e^{-\left(\tau - \frac{i-1}{K_2}\right)(K_1 + K_3)} \right) - K_3 \left(\tau - \frac{i-1}{K_2} \right) \right] \right\} \quad (30)$$

When $K_2 \gg K_3$ we obtain instead of (30)

$$\chi_i \simeq c_0 e^{-\frac{(i-1)K_1}{K_2}} \left\{ K_2 \left(\tau - \frac{i-1}{K_2} \right) e^{-\left(\tau - \frac{i-1}{K_2} \right) K_1} + \frac{K_3}{K_2} \left[2 + K_3 \left(\tau - \frac{i-1}{K_2} \right) \right] \right\} \quad (31)$$

A comparison of the distributions calculated according to Equation (31) (Figure 6) with the corresponding distributions shown in Figures 2 and 3 indicates that the method described, while simple, yields completely satisfactory approximations, particularly in those cases in which the process cannot be reduced to simple chain growth but is complicated by transfer reactions. It is particularly important that the final form of the solution of the problem is in terms of simple exponential functions, i.e., without series or summations.

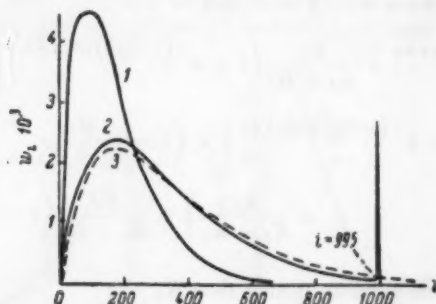


FIG. 6.—1— $K_1 = K_2 = 0.99 \approx 1$, $K_3 = 0.01$, $\tau = 1000$; 2— $K_1 = K_2 = 0.995 \approx 1$, $K_3 = 0.005$, $\tau = 1000$; 3— $K_1 = K_2 = 0.995 \approx 1$, $K_3 = 0.005$, $\tau = 2000$.

Finally let us qualitatively examine polymerization processes in which two other possible limiting mechanisms of chain growth occur: (1) transfer of the active site to solvent and (2) the spontaneous release of the catalyst. It is not hard to see that if δ is small and also if the concentration of monomer is maintained constant during the course of polymerization, these processes are described by a system of equations which can be obtained from equation system (1) by introduction of the new constants $K_1' = K_1 m$ and $K_2' = K_2 m$, and by replacing $K_3 m$ with $K_4' = K_4 S$ or K_5 . The equations obtained in this manner are analogous to those of system (1a), except that the independent variable is not τ but the actual time t . Consequently the form of the equations for MWD is maintained. In cases where the decrease of m in the course of the reaction cannot be neglected, the parameters K_1' and K_2' decrease constantly, becoming equal to zero at the moment of complete consumption of monomer, while K_4' and K_5 do not change appreciably. This indicates that with an increase of δ , the reactions which lead to chain limitation will play a larger role, as a result of which MWD will not take on an equilibrium configuration after complete disappearance of the primary components: their center of gravity will be displaced toward lower degrees of polymerization.

Finally, another complication which can considerably distort the MWD of polymers may be examined. This is the transfer of the reaction to a polymer

in which double bonds able to attach to catalyst exist. In the present paper we shall not show the rather complicated calculations for this case. Experiments indicate that the transfer of the active sites to polymer which leads to chain branching did not play an important role in the reactions we studied.

2. EXPERIMENTAL METHODS AND MATERIALS

We used butadiene or isoprene as the monomer and hexane or ethyl ether as the solvent during polymerization. In addition to a thorough preliminary purification, immediately before polymerization the solvent and the monomer were separately mixed with solutions of butyllithium in a gasoline fraction



Fig. 7.—Reaction ampoule. 1—Sealing points; 2—Striker; 3—Partition; 4—Graduated tube.

(boiling point $> 100^{\circ}$) for at least one half hour (the hexane and ether at room temperatures, the monomer at -10°), after which they were distilled directly into the previously degassed reaction ampoule. The butyllithium was poured from a Shlenk vessel.

Measurement of the rate of polymerization was carried out dilatometrically. In order to improve the removal of heat of reaction, we employed ampoules in which the space filled with solution was made of 10 mm diameter tubing formed into a ring. The other details of the construction are clear from Figure 7.

The sedimentation experiments were carried out in a Svedberg type ultracentrifuge¹⁰ supplied with an optical scale, at 60,000–65,000 rpm. Since hexane and ether are unsuitable for sedimentation experiments because of their high volatility, the samples were dried to constant weight and redissolved in octane saturated with nitrogen. The values of the sedimentation constants were corrected to 20° and 1 atm.^{10, 18} The diffusion experiments were carried out in a Lamm apparatus with an optical scale¹⁰ at a temperature of $20 \pm 0.003^{\circ}$. The average molecular weights were determined according to the Svedberg equation¹⁰. Calculation of the MWD was made by correcting for diffusion accord-

ing to the method suggested by Gosting¹⁵⁻¹⁷. In all sedimentation and diffusion experiments, the initial concentration of the polymer was 0.2 g/100 cm³. Because the molecular weight of the high molecular weight samples alone was of the order of 100,000, concentration corrections were negligible and an extrapolation to infinite dilution was not made. The method and the treatment of sedimentation curves are described in detail in the review of Frenkel¹⁷.

3. EXPERIMENTAL RESULTS AND THEIR ANALYSIS

Samples of polybutadiene and polyisoprene were obtained under thermostated conditions at 30, 50, 60 and 70°. Samples were obtained at the same temperature by polymerization in ethyl ether instead of hexane as a solvent. In order to prevent an excessive increase in viscosity during the course of the polymerization, the concentration of monomer was ≈ 2.3 mole/liter in all experiments. The calculated ratio of the molar concentrations of butyllithium

TABLE I

Sample number	Monomer	Solvent	Polymerization temperature, °C	c_0/m_0 Calculated	δ	$S_{90} \cdot 10^3$	$D_{90} \cdot 10^7$	$M_{w,II}$
1	Butadiene	Hexane	30	1/1200	1	4.0	3.0	132,000
2	Butadiene	Hexane	30	1/1200	1	2.42	—	40,000
3	Butadiene	Hexane	30	1/1200	0.25	1.55	—	13,000
4	Butadiene	Hexane	30	1/1200	0.10	1.3	16	8,000
5	Butadiene	Hexane	30	1/400	1	1.52	—	12,000
6	Butadiene	Hexane	50	1/1200	1	2.96	4.5	65,000
7	Butadiene	Hexane	70	1/1200	1	3.47	—	95,000
8	Butadiene	Ethyl ether	30	1/1200	1	1.94	8.7	22,000
9	Isoprene	Hexane	30	1/1200	1	4.65	3.6	127,000
10	Isoprene	Hexane	30	1/1200	1	2.92	7.26	40,000
11	Isoprene	Hexane	30	1/3000	1	3.8	5.2	72,000
12	Isoprene	Hexane	30	1/3000	0.20	2.54	7.9	32,000
13	Isoprene	Hexane	30	1/400	1	1.76	11.0	16,000
14	Isoprene	Hexane	50	1/1200	1	3.1	7.0	44,000
15	Isoprene	Hexane	50	1/1200	1	4.1	—	100,000
16	Isoprene	Hexane	60	1/1200	1	3.25	6.5	50,000
17	Isoprene	Hexane	70	1/1200	1	4.1	3.64	110,000
18	Isoprene	Hexane	70	1/1200	1	3.32	5.15	64,000
19	Isoprene	Ethyl ether	30	1/1200	1{	2.5	—	30,000
						3.24	—	55,000

to monomer c_0/m_0 was 1/400 for two samples, 1/3000 for two samples, and 1/1200 for all others. However, it should be noted that the actual ratio could in a number of cases differ somewhat from the calculated for several reasons; errors in the determination of the concentration of butyllithium, inaccuracy in the concentration of the components, and the presence of traces of inhibiting substances. The important information about the preparation of the polymer samples, and data obtained on them are given in Table I. M. N. Barsukova participated in preparing the samples.

All samples were studied with the ultracentrifuge preparatory to obtaining the MWD. However, it became evident that calculation of distributions from experimental data was practically impossible for specimens prepared by polymerization in pure hexane, since the polydispersity of such polymers is exceptionally small and is outside the resolution of the ultracentrifuge (the broadening of sedimentation curves as a result of diffusion far exceeded that resulting from polydispersity). It is known^{17,18} that for a polydisperse substance the relation $\xi^2/2t = f(r^2t)$ (where ξ^2 is the square of the standard deviation of the sedimentation curve, r the distance from the rotor center, and t the

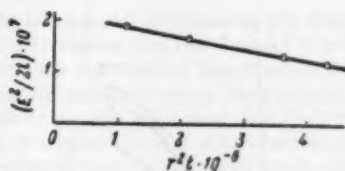


FIG. 8.

time) describes a straight line from whose positive slope the standard deviation of the MWD may be calculated.

For a monodisperse polymer, the graph either must be parallel to the abscissa, separated by a distance of $\xi^2/2t = \alpha_t D$ (α_t is a temperature correction) or possess a small negative slope which increases with the increase of the concentration dependence of S^{12} . Figure 8 shows such a graph for specimen 1, which gives evidence in accordance with the above, that this specimen is practically monodisperse. Analogous results were obtained for other samples prepared in hexane.

Figure 9 illustrates the sedimentation curves for specimen 9 taken at several successive time intervals.

On the basis of the sedimentation data and the analysis of the MWD shown above, we may conclude for the polymerization of butadiene or isoprene with butyllithium in hexane at temperature from 30–70° that the role of secondary reactions leading to the limitation of chain growth is quite small and may be neglected. This would mean that almost all chains grow until the monomer is consumed. The MWD is obviously close to the values shown in Figure 1 (Curves 3 and 4), the polydispersity being small and of the order produced by statistical distribution of the dimensions of individual chains. The relation

$M = \delta \frac{m_0}{c_0} M_0$ is fulfilled within the limits of error in the majority of cases.

It should be noted that the above does not fully agree with the results of earlier rate measurements²⁰. According to the latter, the ratio K_1/K_2 is of the

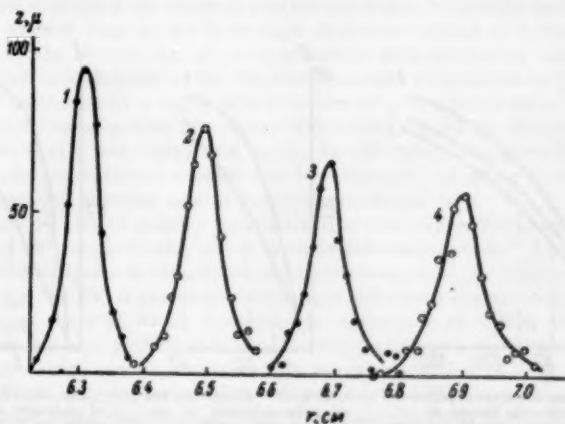


FIG. 9.—1— $t=3600$ sec.; 2— $t=5100$ sec.; 3— $t=6700$ sec.; 4— $t=8600$ sec.

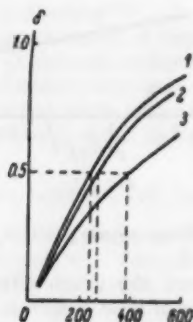


Fig. 10.—Kinetic curves of polymerization for butadiene in hexane at 30°. Abcissa: time, min. 1— $M = 12,000$; 2— $M = 30,000$; 3— $M = 130,000$.

size 0.01–0.02 for polymerization at complete conversion. But the MWD in this case would remain quite narrow, would possess considerable polydispersity, and would be rather asymmetric, with a more gentle slope in the low molecular weight region (Figure 1, curve 2). Asymmetry of this kind would be even more pronounced in the sedimentation curves. The latter are, however, symmetrical for all polymerizations carried out in hexane (Figure 9) and the broadening, as pointed out above, is caused principally by diffusion. The problem of the sources of discrepancy between polymerization rate data and the sedimentation data requires further study.

On the basis of a large amount of experimental material one of us^{20, 21} has established earlier that there is no direct proportionality between c_0 and the overall rate of polymerization at a given value of m_0 during the polymerization of isoprene. With an increase in the temperature of polymerization, this phenomenon begins to appear at large values of c_0 . An analogous situation is found during the polymerization of butadiene. Thus, as follows from the rate curves of Figures 10 and 11 for polymerization at 30°, even a ten-fold increase

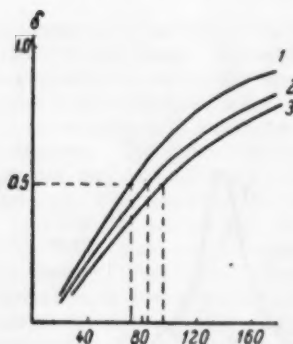


Fig. 11.—Kinetic curves of polymerization for isoprene in hexane at 30°. Abcissa: time, min. 1— $M = 16,000$; 2— $M = 40,000$; 3— $M = 65,000$.

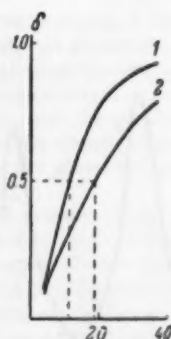


Fig. 12.—Kinetic curves of polymerization of isoprene in hexane at 50°. Abcissa: time, min. 1— $M = 50,000$; 2— $M = 100,000$.

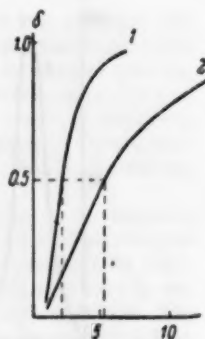


Fig. 13.—Kinetic curves of polymerization of isoprene at 70°. Abcissa: time, min. 1— $M = 64,000$; 2— $M = 110,000$.

of c_0 (corresponding to an equal decrease of M), leads only to an insignificant increase of the overall reaction rate (for $\delta = 0.5$ it is 1.5 times). It is obvious from the case given that a reversible deactivation mechanism is the only acceptable explanation for this interesting phenomenon in which all centers discontinue or delay their growth for a time and then renew it again with equal probability. Thus it is possible that active molecules, interacting with each other or with the catalyst, periodically form small active metal organic sites of complex structure. After the dissociation of such compounds, chain growth is resumed.

One can also arrive at an interpretation of this phenomenon from a somewhat different point of view. Let us recall that the R-Li bond on which the subsequent attachment of monomer to the active sites occurs is strongly polarized and represents effectively an electric dipole. Such dipoles attempt to assume a mutual orientation in which their energy would be minimal; they associate to form multipoles. In view of the fact that one of the stages of the attachment of monomer to the growing chain is the polarization of the monomer in the dipole field of the active site, it is evident that the weakening of this field by

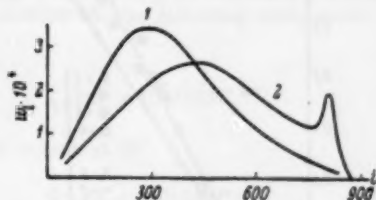


Fig. 14.—1—MWD of polybutadiene; 2—MWD of polyisoprene.

adjacent dipoles leads to a decrease in the probability of attachment; i.e., to a retardation of chain growth. On the other hand, the association of the dipoles is constantly disturbed by thermal motion in different directions. If the concentration of active sites (dipoles) is higher, the bonds between them which have been disturbed by thermal motion are more frequently restored and the average growth rate of the individual molecular chains is lower. Thus, the increase in the overall rate of polymerization with increasing concentration of active sites is counteracted by the simultaneous retardation of the growth of polymer molecules as a result of interaction of active polar sites. With an increase of the temperature of polymerization the role of the thermal motion increases so that a weakening and finally an effectively complete disturbance of the interaction between dipoles can be expected, resulting in restoration of proportionality between rate of polymerization and c_0 .

Figures 12 and 13 present polymerization rate curves for isoprene in hexane at 50 and 70°, respectively, which confirm this assumption. At 50° the interaction of the dipoles is already considerably weaker in the interval of c_0 values studied, and at 70° it practically no longer influences the kinetics.

In those cases in which electrostatic interaction of active sites cannot be neglected, the true growth rate (K_2) corresponding to a particular polymerization temperature can be obtained only by extrapolation to $c_0 = 0$.

The above interpretation of the characteristic differences in polymerization kinetics obviously does not contradict the results of the sedimentation experiments. Indeed, since the interaction between the active sites delays the growth

of all chains equally, it does not have to lead to a noticeable increase in the polydispersity in the MWD.

As was pointed out, in some polymerization experiments ethyl ether was used as a solvent instead of hexane. It is known that the addition to the reaction mixture of even minute quantities of a number of simple ethers²² of or certain other compounds²³ accelerates polymerization. It is presumed that these substances form complexes with the metal organic bond, causing a screening of the metal cation so that the bond between the organic anion and the metal cation becomes more mobile. As a result, the overall rate of polymerization increases greatly.

Figure 14 shows MWD of polybutadiene (curve 1) and polyisoprene (curve 2) obtained by polymerization in ethyl ether at 30° (calculated $c_0/m_0 = 1/1200$; $\delta = 1$). In contrast to polymers obtained in hexane, these polymers are quite polydisperse, indicating the presence of secondary reactions leading to chain limitation. Such reactions are most likely transfers of the active site to

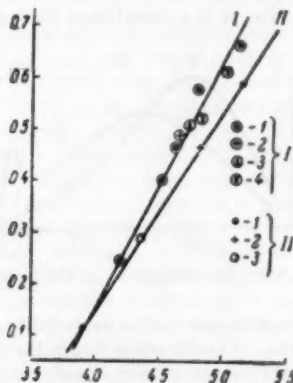


FIG. 15.—Abscissa: $\log M$. Ordinate: $\log S-13$. I. Polyisoprene, polymerization in hexane at: 1—30°, 2—50°, 3—60°, 4—70°. II. Polybutadiene; 1 and 2—polymerization in hexane at 30 and 50°; 3—in ethyl ether at 30°.

monomer or the kinetically equivalent reaction of dissociation of the active site with the release of catalyst together with monomer. Considering that the relation c_0/m_0 in both cases is close to 1/1000, and comparing curves 1 and 2 in Figure 14 with the model distribution shown on Figure 2 and 3, it can be assumed with sufficient confidence that K_1/K_2 is equal to 0.005–0.006 in the first case and to 0.003–0.004 in the second case.

The nature of these distributions indicates on the one hand that the coordination complex with the ether makes the bond on which the addition of monomer units occurs more active catalytically, while at the same time such coordination weakens the bond, so that the bond may break and so release the complex from the polymer chain.

It has been shown by a number of authors^{22, 24} that the microstructure of the polybutadiene and polyisoprene chains (correlation of the quantities of 1,2 and 1,4 configurations) obtained with metal organic catalysts is determined to a considerable degree by the conditions of the polymerization and the composition of the catalyst. In polybutadiene obtained by polymerization with butyl-

lithium in ethyl ether at 30°, the quantity of 1,2 structure is 70% as compared to 15% in polymerization in hexane.

The same results are obtained in isoprene polymerization. With increasing temperature of polymerization, some increase in the amount of 1,4 structure is also found. In Figure 15 $\log S$ is plotted against $\log M$ for polybutadiene and polyisoprene samples obtained under various conditions.

It is seen that the points for one type of polymer all lie on the same line. This provides evidence that the hydrodynamic properties of the macromolecules depend only in a minor way on the microstructure of the molecular chains. This is evidently explained by the fact that, during the increase in the amount of 1,2 structure with the corresponding shortening of the molecular chain, the mobility of individual chains decreases so that the dimensions of the molecular aggregate in solution remain unchanged. The second important conclusion is that increasing the temperature of polymerization to 70° and employing ether as the solvent does not lead to a noticeable increase in chain branching, since a single relation $S = f(M)$ for a given type of polymer would otherwise not be very likely.

The relation between S and M may be expressed analytically for the ranges of molecular weight studied by the following expressions (S is expressed in svedbergs):

For polybutadiene

$$S = 0.0389M^{0.20}$$

For polyisoprene in octane at 20°

$$S = 0.0155M^{0.40}$$

Considering that a larger exponent of M indicates less flowing of solvent through the molecular aggregates, it should be presumed that the polyisoprene molecules wind into more dense aggregates in octane than do the polybutadiene molecules.

We wish to take this opportunity to express our deep gratitude to M. N. Barsukova for cooperation and help and also to S. Ya. Frenkel for evaluation of the results and valuable observations.

SUMMARY

Problems connected with the calculation and analysis of molecular weight distributions of polymers obtained by catalytic polymerization were examined. An approximate method of calculation was proposed which is unique in its simplicity and which gives good approximations in the majority of cases of practical interest.

Experimental data from a study of samples of polybutadiene and polyisoprene prepared by polymerization in solution by means of butyllithium were considered. The low degree of polydispersity for these polymers was noted in particular.

REFERENCES

- ¹ Staveland, F. W., and others, *Ind. Eng. Chem.* **48**, 778 (1956); Horne, S. E., and others, *ibid.* 784 (1956).
- ² Robertson, R., and Marion L., *Can. J. Research* **26**, 657 (1948).
- ³ Morton, A. A., Patterson, G. H., Donovan J. J., and Little E. L., *J. Am. Chem. Soc.* **69**, 160 (1947).
- ⁴ Morton, A. A., and Brown, M. L., *J. Am. Chem. Soc.* **69**, 160 (1947).
- ⁵ Morton, A. A., and Letsinger, R. L., *J. Am. Chem. Soc.* **69**, 172 (1947).

- ⁶ Natta, G., Pino, P., Mantica, E., Danusso, F., Massanti, G., and Peraldo, M., *Chim. e ind. (Milan)*, No. 2, 124 (1956); *C.A.* **50**, 9056d.
- ⁷ Natta, G., *Angew. Chem.* **68**, 393 (1956).
- ⁸ Mamontova, O., Abkin A., and Medvedev, S., *Zhur. Fiz. Khim.* **14**, 36 (1940).
- ⁹ Ziegler, K., Holzkamp, E., Breil, H., and Martin, H., *Angew. Chem.* **67**, 426, 541 (1955).
- ¹⁰ Dostal, H., and Mark, H., *Z. Physik. Chem.* **B29**, 299 (1935).
- ¹¹ Marei, F., *Acta Physicochim. URSS* **9**, 741, 759 (1938).
- ¹² Ginell, R., and Simha, R., *J. Am. Chem. Soc.* **65**, 706, 715 (1943).
- ¹³ Slutskii, E. E., Tables for the Calculation of Incomplete Γ -functions (in Russian) (Izd. AN SSSR, 1950).
- ¹⁴ Svedberg T., and Pedersen, K., *The Ultracentrifuge*, Oxford, 1940.
- ¹⁵ Frenkel, S. Ya., *Zhur. Tekh. Fiz.* **24**, 2169 (1954); *C.A.* **49**, 13741b.
- ¹⁶ Gosting, L., *J. Am. Chem. Soc.* **74**, 1548 (1952).
- ¹⁷ Frenkel, S. Ya., *Uspekhi Fiz. Nauk.* **53**, 161 (1954); *C.A.* **49** 11316i.
- ¹⁸ Williams, J. W., Baldwin, R. L., Saunders, W. M., and Squire, P. G., *J. Am. Chem. Soc.* **74**, 1542 (1952).
- ¹⁹ Baldwin, R., *Biochem. J.* **65**, 503 (1957).
- ²⁰ Korotkov, A. A., Proceedings of the International Symposium on High Molecular Weight Compounds, Prague (in Russian) (1957).
- ²¹ Korotkov, A. A., Chesnokova, N. N. and Trukhmanova, L. B., Collection of Theses and Papers of the 9th Conference on General Aspects of the Chemistry and Physics of High Molecular Weight Compounds, (in Russian) (Moscow, January, 1957), p. 31.
- ²² Piotrovskii, K. B. *ibid.*, p. 51.
- ²³ Morton, A. A., Brown, M. L. and Magat, E., *J. Am. Chem. Soc.* **69**, 161 (1947).
- ²⁴ Meyer A. W., Hampton R. R., and Davison, J. A., *J. Am. Chem. Soc.* **74**, 2294 (1952).

THE MECHANISM OF ISOPRENE POLYMERIZATION INITIATED WITH TiCl_4 -TRIALKYLALUMINUM. MOLECULAR WEIGHT DISTRIBUTION OF THE POLYMER *

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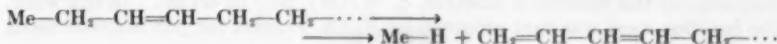
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One of the important problems of the modern physical chemistry of polymers is the mechanism of polymerization catalyzed by the complexes of aluminum alkyls with the chlorides of metals of the transition groups (Ti, V and others). In a number of researches devoted to this question^{1, 2} it has been shown that the addition of monomer to a growing chain proceeds on strongly polarized metal carbon bonds, ($\text{Me}^+ - \text{C}^-$), at the surface of a solid phase formed by partially reduced transition metal chlorides. It has also been found that the average molecular weight of the polymer is practically independent of the duration of the polymerization which indicates rapid growth of active sites and the presence of reactions which limit the chain. An opinion is expressed¹, that reactions for limiting chains in the polymerization of α -olefins could be:

1. Replacement of the polymer chain by an active monomer bond with transfer of a hydrogen atom from the chain to the monomer.
2. Direct transfer of a hydrogen atom from the end of the polymer chain to the surface of metal catalyst complex. In either case there is formed a macromolecule with a vinylidene end group and in its place new chain growth can occur, assuming that $\text{Me}^+ - \text{H}$ is also capable of adding monomer.

Theoretical weight, molecular weight distributions (MWD), calculated for analogous mechanisms for chain growth limitation on the assumption that the probability of limiting action is independent of the molecular weight of the chain, are characterized by one maximum and a long tail in the direction of high molecular weight. The number MWD decreases exponentially with increasing molecular weight³.

MWD of low pressure polyethylene determined by fractionation of polymers are of the shape⁴ conforming with the above assumptions concerning chain scission during catalytic polymerization. But the result of this work cannot be applied to the polymerization of other monomers, especially dienes. The latter would be less susceptible to reactions limiting chain growth than ethylene or α -olefins. It is actually possible, in catalytic polymerization, for limiting reactions to proceed with transfer of hydrogen atoms from macromolecules to active sites. But in the case of dienes this role can be played only by the fourth hydrogen from the end of the carbon chain; for example:



* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY from *Zhur. Tekh. Fiz.* 28, 2487-2492 (1958).

Such a process is apparently much less probable than with olefins where the necessary hydrogen is furnished by the second carbon. For example, the polymerization of butadiene and of isoprene with butyllithium in a saturated hydrocarbon medium proceeds with almost complete absence of chain growth limiting reactions⁶.

The present work discusses some details of the mechanism of polymerization of isoprene catalyzed by complexes formed from reaction of TiCl_4 with triisobutylaluminum, on the basis of analysis of MWD by means of the ultracentrifuge.

EXPERIMENTAL METHODS AND MATERIALS

As solvents for polymerization of isoprene, isopentane and benzene were used. The initial concentration of monomer in all experiments was 50% by volume. In addition, experiments were carried out on polymerizing monomers without solvent.

All of the samples described in this work were obtained using a 1:1 mole ratio of catalyst components. The mole ratio of monomer to each catalyst component was 3000 for polymerization of pure monomer and 1500 for polymerization in solution.

The ampoule in which the polymerization was carried out was divided into two parts by a thin partition. Into one section, previously well purified monomer and solvent were distilled. The other section was filled with catalyst components introduced from a Shlenk container. In a number of experiments one catalyst component was added to the monomer. At the right moment, the partition was broken by a striker inside the ampoule and the reaction components were mixed. The polymerization temperature in all experiments was about 32°.

In order to obtain the most even distribution of catalyst particles in the medium the ampoule was continuously shaken by means of a vibrator during reaction. The resulting polymer dissolves and the viscosity of the medium increases in proportion to the amount of conversion.

The reaction was terminated by the addition of methanol which immediately destroys the catalyst and simultaneously precipitates the polymer from solution. Molecular weights and MWD were determined by measuring the sedimentation speed in an ultracentrifuge at 40,000 rpm ($\approx 120,000$ g). Polymer solutions in octane at a concentration of 2 mg/ml (0.2%) were used for conducting the sedimentation experiments.

For conversion of the sedimentation constant, measured at the final concentration, to true molecular weight (M) it is necessary to measure independently the second virial coefficient, B_2 . Then the following formula can be used:

$$M = \frac{M_e}{1 - 2B_2cM_e} \quad (1)$$

where M_e is the so called "apparent" molecular weight, determined by the Svedberg formula in which the values of S_e and D_e determined at the final concentration, C , are substituted. After M has been determined for some polymer homologs by this method, a function, $S_e = f(M)$, may be set up. In this work, the function used was that obtained by S. Ya. Frenkel for polyisoprene using the above method:

$$S_{2\text{mg/ml}} = 0.372 M^{0.51} \quad (2)$$

TABLE I

THE BASIC POLYMERIZATION DATA, DESCRIPTION OF SAMPLES, RESULTS OF SEDIMENTATION EXPERIMENTS. VALUES OF S AND M CORRESPOND TO MAXIMUM VALUES FROM EXPERIMENTAL DIAGRAMS

No. of Sample	Method of polymerization	Time of polymerization	Degree of conversion	S_{max}/m	M	Remarks
1	Without solvent	1.5 min	1	7.50	1,600,000	
2	Without solvent	6 min	6	7.25	1,400,000	
3	Without solvent	20 min	13	7.45	1,560,000	
4	Without solvent	20 min	14	7.37	1,500,000	
5	In isopentane	30 min	24	7.60	1,750,000	
6	In benzene	25 min	18	7.80	1,900,000*	
7	In benzene	≈ 10 h	30	7.50	1,600,000*	
8	Without solvent	125 min	10	7.60	1,750,000*	Triisobutylaluminum
9	Without solvent	≈ 8 h	30	7.0	1,300,000*	added with the monomer

* MWD not unimodal. The molecular weight given in the table corresponds to the major component.

This function is valid when $M > 10^5$, which is true in the present case. The methods of calculation of the sedimentation diagram and obtaining the MWD are described in detail in a review⁶.

EXPERIMENTAL RESULTS AND DISCUSSION

From Table I it follows that over a wide range of degree of conversion, down to the smallest practical one (Sample 1), the molecular weights of the polymers are equal within experimental error. Thus, the interval of time from the moment of inception of an active chain until its deactivation (accompanied by detachment of a polymer molecule from an active site and its dissolution) can be calculated in fractions of a minute. Therefore, in these systems a fixed MWD is established almost immediately. If there were limitation of growth occurring by one of the known transfer mechanisms, as was stated above, there would be expected a polydisperse distribution, independent of degree of conversion, with a predominance of low molecular weight components and a characteristic high molecular weight tail. But the actual distributions were different. Together with the absence of dependence on degree of conversion, the distributions were characterized by symmetry; comparatively little relative



FIG. 1.—Experimental sedimentation diagram of sample 3. 4— $t = 42$ min, 3— $t = 56$ min; 2— $t = 75$ min; 1— $t = 90$ min.

dispersion, $\Delta M/M = 0.2 - 0.3$ where ΔM is the standard deviation of the MWD. They were displaced to the high molecular weight region with macromolecules having molecular weights below 400,000 being practically absent in most cases (Figures 1 and 2). There appears to be a contradiction here: on the one hand a reaction is taking place limiting the molecular chains; on the other hand, the MWD does not correlate with any of the known kinetic schemes which take this reaction into account. Here it must be remembered that in the usual calculation of the theoretical MWD the probability of the occurrence of the chain limiting reaction is assumed to be independent of the molecular weight of the chain. Hence, there is obtained an exponential decrease of the MWD values on the high molecular weight side. In the cases shown here, this premise is not true. The data obtained indicate the need to search for a mechanism of chain detachment the rate of which is strongly dependent on the size of the chain and where there is little probability that the macromolecule will become detached from the catalyst complex until it reaches sufficient length (about 7000 units). The explanation must be sought in the specific heterogeneous polymerization process. Indeed, in any homogeneous polymerization the catalyst has no influence on the mobility of molecular segments or on the polymer molecule as a whole. Heterogeneous polymerization is altogether different in that the growing chain exists on the surface of a solid phase on which it is bound by active metal-carbon bonds. If the active sites are located close to one another on the surface, the growing macromolecules are tightly packed, forming a crystalline surface. Consequently, they do not possess the degree of freedom associated with rotation of segments. In the case where the active sites are remote from each other and the growing chains do not overlap, the number of configurations which can exist is limited because of the adsorption of chains on the catalyst surface. Thus the detachment of a polymer molecule from the catalyst and its dissolution will always be accompanied by an increase in the configurational entropy ΔS , determined by the following equation:

$$\Delta S = \frac{k}{2} \nu = \frac{k\alpha}{2 M_0 r} M \quad (3)$$

where ν = number of rotational degrees of freedom mobilized in transferring the macromolecule into solution;

k = Boltzmann constant;

r = Number of chemical units in one kinetic unit (segment);

M_0 = molecular weight of monomer;

α = A parameter, changing within the limits of 0 to 1, which takes into account the degree of decrease of mobility of the molecular segments at the surface.

At the same time energy must be expended in desorption of the macromolecule from the surface of the catalyst; an amount ΔU , determined by the energy of breaking the active bond. The change of free energy of the reaction of detaching the macromolecule from the active complex is given by the following equation:

$$\Delta F = \Delta U - \frac{kT\alpha}{2M_0 r} M \quad (4)$$

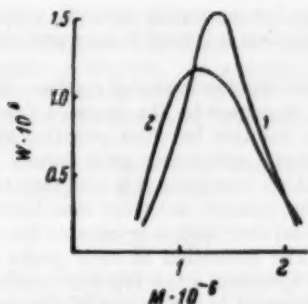


FIG. 2.—Weight MWD. 1—Sample 1; 2—Sample 3.

The value of ΔU , in the first approximation, does not depend on the number of units or the molecular weight of the polymer molecule (the heat of solution of polyisoprene in hydrocarbon is nearly zero). Therefore, it follows from Equation (4) that ΔF decreases with an increase in M . This means that with respect to growth of the molecular chain, the probability of detachment from the catalyst is given by

$$e^{-\frac{1}{KT} \left(\Delta U - \frac{kT\alpha}{2 M_0 r} \right) M}$$

and that a macromolecule will preferentially detach from the catalyst with the attainment of a molecular weight which satisfies the condition $(kT\alpha/2 M_0 r) \times M \simeq \Delta U$. This is the mechanism that we propose for the limitation of molec-

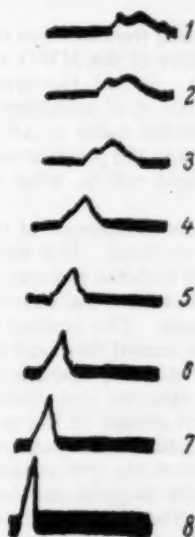


FIG. 3.—Experimental sedimentation diagram, sample 9. 8— $t = 14$ min; 7— $t = 33$ min; 6— $t = 50$ min; 5— $t = 70$ min; 4— $t = 84$ min; 3— $t = 126$ min; 2— $t = 140$ min; 1— $t = 160$ min.

ular chain growth in the heterogeneous catalytic polymerization of isoprene. On the basis of this mechanism it is easy to interpret the above described characteristic MWD.

It should be noted that the fundamental reaction on the catalyst surface in this case could possibly be caused by the common deactivation processes with this difference; that the reaction becomes probable only after the molecular weight of the chain reaches a sufficiently great value.

On the basis of the above reasoning it is also easy to interpret a polymodal MWD, consisting of a few (usually not more than three) peaks (Figures 3 and 4). Each peak of the total distribution represents the spread of separate quite narrow distributions. The formation of such peaks is evidently connected with the presence in the system of a few types of catalyst complexes characterized particularly by differences in the values of the energy, ΔU , which determines the molecular weight range in which the detachment of macromolecules from the catalyst takes place.

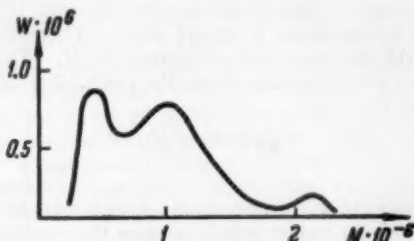


FIG. 4.—Weight MWD, sample 9.

If molecular chains originating from reaction at different active sites are not similar in structure, stratification of the MWD will take place even when the sites have the same ΔU values. In fact, the structure of the chain determines its rigidity (that is, the number, r , of monomer units composing one kinetic unit) and consequently affects the value of ΔF (Equation 4). The less the freedom of rotation of segments in the polymer molecule, that is the larger r is, the higher the molecular weight will be when detachment from the active surface takes place.

The possibility of simultaneous existence of different types of structure at the active sites can hardly be doubted. It is well known, for example, that in the catalytic polymerization of α -olefins isotactic and amorphous polymers are formed at the same time and that this is associated with the presence of different structures of catalyst complexes. The number of components of a complex distribution does not, as a rule, exceed three and they are usually well resolved. This last condition indicates stepwise changes in the properties and in the chemical structure of these catalytic complexes. These differences can be caused by different substituent groups on the metal atom forming the active bond and also by the microstructure on the catalyst surface adjoining the active bond. The presence of benzene in the system and also the preliminary reaction of one catalyst component with isoprene can contribute to the formation of different complex structures. Therefore, MWD composed of a few components are especially characteristic of polymers obtained by polymerization in benzene and of systems in which one component of the catalyst is added to the monomer.

The calculation of distribution has been made on the assumption that differences in microstructure of the molecular chains (if they exist) do not strongly influence the hydrodynamic properties. As a result, the one function, $M = f(S)$, can be used for all components of the MWD.

The accuracy of such an assumption for isoprene and for butadiene polymers has been previously proved⁵.

The authors express their thanks to A. A. Korotkov and M. A. Krupyshev for their assistance and interest in this work.

SUMMARY

The molecular weight distribution of polyisoprene obtained by polymerization under the influence of complexes of titanium tetrachloride with triisobutylaluminum has been found within broad limits to be independent of the degree of conversion. On the basis of this finding an hypothesis is offered to explain the limitation of polymer chain length according to which chain scission is assumed to increase with the size of the chain.

REFERENCES

- ¹Natta, G., Pino, P., Mantica, E., Danusso, F., Mazzanti, G. and Peraldo, M., *Chim. e Ind. (Milan)* **38**, 124 (1956); *C. A.* **50**, 9056d.
- ²Eirich, F. and Mark, H., *J. Colloid Sci.* **11**, 748 (1956).
- ³Frith, E. M. and Tuckett, R. F., *Linear Polymers*, p. 96 (1951).
- ⁴Wesslau, H., *Makromol. Chem.* **20**, 111 (1956); *C. A.* **50**, 16290b.
- ⁵Bresler, S. E., Korotkov, E. E., Mosevitskii, M. I. and Poddubnyi, I. Ya., *Zhur. Tekh. Fiz.* **28**, 114 (1958); *C. A.* **52**, 15112g.
- ⁶Frenkel, S. Ya., *Uspekhi Fiz. Nauk* **52**, 161 (1954); *C. A.* **49**, 11316i.

KINETICS OF ISOPRENE POLYMERIZATION INITIATED WITH TiCl_4 —TRIALKYL ALUMINUM *

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For the study of the mechanism of polymerization by means of complexes of aluminum organic compounds with titanium chlorides, data on the kinetics of polymerization is of great interest. Up to the present time, the rate of polymerization of propylene has been studied^{1,2} but the interpretation of the kinetic data is difficult because the polymer, which is practically insoluble in the reaction medium, entraps the catalyst resulting in a rate of reaction which is dependent on the diffusion of monomer through the polymer to the active sites.

In this work the polymerization of isoprene, which yields polymers soluble in the monomer, in saturated hydrocarbons and in benzene, was studied. The rate of the polymerization reaction was measured by the thermal effect in a calorimeter consisting of a 3.5 l. Dewar flask, with a lid, immersed in a thermostated air bath maintained at approximately the temperature of the reaction. Low viscosity spindle oil, heated to the temperature of the reaction (about 32°), served as the calorimeter fluid. The ampoule holder extended outside of the calorimeter and was connected to a shaking apparatus. The ampoule was divided by a thin partition into two sections each holding 45–50 cc. Into one section previously purified monomers and solvent were distilled. The other section was filled with catalyst components from a Shlenk container. The change in temperature of the calorimeter was determined with a Beckman thermometer with an accuracy of 0.01°. When the temperature of the calorimeter containing the ampoule remained constant to within 0.01–0.02° for 30–40 minutes, the shaking apparatus was connected and the partition was broken with a striker. Intensive shaking was continued during the entire experiment resulting in mixing of the reaction mixture and of the calorimeter fluid. The rate of reaction was determined by the rate of heat evolution; in other words, by the temperature rise in the calorimeter. For a rise of 0.1–0.5° the reaction conditions remained practically isothermal. This rise permits the kinetics of the reaction to be observed with sufficient accuracy. Adiabaticity of the calorimeter and the effect of mechanical heat were controlled in separate experiments.

Figure 1 shows a number of curves of the kinetics of polymerization of isoprene under the influence of titanium tetrachloride and triisobutyl aluminum (1:1 relative proportions of catalyst components) with preliminary formation of the active complex in one section of the ampoule. It is noticed first that the polymerization rate is maximum immediately after reaction of monomer with catalyst. A noticeable decrease in rate normally take place at a rather low degree of conversion (10–20%) that cannot be explained by decrease in monomer concentration. Neither can it be explained by trapping of the catalyst parti-

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY from *Doklady Acad. Nauk SSSR* 121, 859–861 (1958).

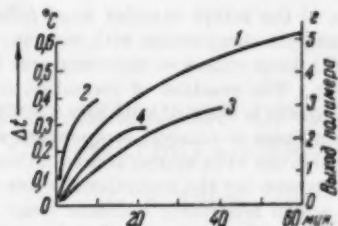


Fig. 1.—Kinetic curves when premixed catalyst is introduced into the reaction mixture. 1.—Without solvent, each component of the catalyst, 0.00012 mole; 2.—Without solvent, each component of the catalyst, 0.00048 mole; 3.—50% solution in isoprene, each component of the catalyst, 0.00012 mole; 4.—50% solution in benzene, each component of the catalyst, 0.00012 mole. Abscissa: Minutes. Right ordinate: Yield of polymer. Left ordinate: Δt , $^{\circ}\text{C}$.

cles by polymer because the polymer is soluble. Possible reasons are chemical change of the catalyst surface or poisoning by byproducts of the polymerization reaction.

Peculiar results are obtained by separate introduction of the catalyst components into the reaction medium (one of the components introduced with the monomer). In this case the course of the reaction is very different. The polymerization proceeds very slowly for the first 30–40 minutes and the heat evolved is hardly noticeable. Furthermore, during this period some absorption of heat takes place, apparently connected with the formation of the catalyst complex (Figure 2). Following the induction period there is a practically linear increase in temperature accompanied by a corresponding accumulation of polymer. But in this period polymerization is slower than with the same amount of premixed catalyst. Another important occurrence takes place when catalyst components are introduced separately. In this case the reaction mixture is a transparent red-brown liquid which deepens in color as the reaction proceeds. Only the strong Tindall effect, appearing on illumination of the ampoule with a narrow beam of light, shows that the catalyst is not dissolved in the medium but exists as a very finely dispersed colloid.

Detailed interpretation of the peculiarities of the polymerization on separate introduction of the catalyst requires additional experiments, but the major role of the reaction of isoprene with the catalyst components is now obvious. In particular, the occurrence of this reaction is demonstrated by the appearance of a yellow coloring of monomer on addition of even a small quantity of TiCl_4 to it. It would be a mistake to think that the monomer reacts only with the catalyst component which is added first; the second component, which is located in the separate section of the ampoule and hence is not connected with the complex, can apparently react with the monomer after destruction of the partition.

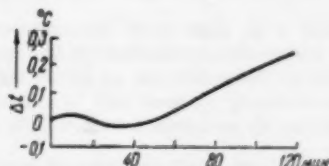


Fig. 2.—The kinetic curve when triisobutyl aluminum is introduced with the monomer. Polymerization without solvent; each component of the catalyst, 0.00012 mole. Abscissa: Minutes. Ordinate: Δt , $^{\circ}\text{C}$.

Thus, the formation of the active complex must follow the dissociation of the complexes of the catalyst components with isoprene. This process takes place in the presence of a large excess of monomer and therefore takes a considerable length of time. The reaction of formation of catalyst complex is exothermic, but in this case it is coupled with the endothermic reaction of dissociation of primary complexes of catalyst components with monomer, resulting in a total reaction which can even appear somewhat endothermic (Figure 2).

From the above the reason for the exceptionally fine dispersion of catalyst when components are added separately becomes clear. Actually, the usual method of preparing the catalyst in a small volume immediately produces many centers of crystallization which grow vigorously and fuse with each other in the microscopic precipitate. In the present case, as is clear from the above description, the process proceeds much more mildly and in larger volume. Of special significance is the fact that the catalyst formation takes place in the presence of the monomer. Because of this, immediately after formation of particles of active catalyst polymer molecules begin to grow on their surfaces screening the particles from each other and making further aggregation difficult.

It is interesting to note that in polymerization of isoprene in benzene using coarse catalyst dispersion prepared in advance, the catalyst soon becomes colloidally dispersed and the mixture has the same appearance as when the catalyst components are introduced separately. Such dispersive action of the benzene is probably connected with its complex forming properties. Under these conditions the polymerization is greatly delayed (Figure 1, 4), corresponding to the general tendency toward decrease of activity of colloidal catalysts.

In addition to the kinetic studies, molecular weight distributions of the polyisoprenes isolated at different degrees of conversion using the complex catalyst were studied together with I. Ya. Poddubnyi and N. N. Chesnokova³. It was established that the average molecular weights and molecular weight distributions, within limits, are practically independent of the degree of conversion. There is also a hypothesis proposed concerning the mechanism of limitation of growth of chains leading to the comparatively narrow and symmetrical molecular weight distribution.

The authors express their thanks to N. N. Chesnokova for her assistance with this study.

REFERENCES

- ¹ Natta, G., Pasquon, I. and Giachetti, E., *Angew. Chem.* **69**, 213 (1957).
- ² Natta, G., Pasquon, I. and Giachetti, E., *Makromol. Chem.* **24**, 258 (1957); *C. A.* **62**, 3491c.
- ³ Bresler, S. E., Mosevitskii, M. I., Poddubnyi, I. Ya. and Chesnokova, N. N., *Zhur. Tekh. Fiz.* **28**, 2487 (1958).

THE CRYSTALLIZATION OF MODIFIED CIS-POLYBUTADIENE *

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A previous note¹ described experimental results on the crystallization of a sample of polybutadiene with a high *cis*-1,4 content and mentioned results on cured and isomerized samples. The present paper describes in detail measurements made on peroxide-cured samples and on samples in which the *trans*-1,4 content has been increased by isomerization. The purpose of these measurements has been to establish the effectiveness of the introduction of various types of points of disorder in retarding or preventing the formation of crystals.

SAMPLE PREPARATION

Isomerized samples.—Although it is possible, by adjustment of polymerization conditions, to prepare samples of *cis*-polybutadiene with varying *cis*, *trans*, and vinyl contents, it appears that in some cases the copolymer units do not occur in a truly random fashion. Consequently, samples of varying *cis* content were prepared by isomerization of the high *cis*-1,4 polymer described previously¹. The method of isomerization was similar to that described by Golub². Diphenyl disulfide was employed as photosensitizer, and the amount of sensitizer and time of irradiation were adjusted to produce a series of samples with increased *trans* content. The microstructure was determined from infrared measurements³.

Crosslinked samples.—Samples of the original polymer were crosslinked by treatment with di-*tert*-butyl peroxide. The polymer sample was pressed out in a thin sheet and allowed to absorb peroxide vapor in a closed vessel for 16 hr. The samples were cured at 260° F in the usual manner. The values of M_c were calculated from swelling measurements in benzene on the basis of a value of $\mu = 0.44$ obtained from osmotic measurements. No correction was applied to allow for the finite molecular weight of the starting material, which was found from osmotic measurements to be approximately 250,000. Due to uncertainties in the calculation of M_c values from swelling measurements⁴, these values must be taken as only approximate.

EXPERIMENTAL MEASUREMENTS

Crystallization measurements were made in a dilatometer in the usual manner⁵. Typical sigmoidal crystallization rate curves were obtained, and the crystallization isotherms could be superimposed by shifting along the time axis⁶. Although Mandelkern⁷ has recently pointed out that polybutadiene copolymers containing 80% *trans*-1,4 structure do not exhibit this property of

* Reprinted from the *Journal of Polymer Science*, Vol. 41, No. 138, pages 213-217 (1959). Presented at the Eighth Canadian High Polymer Forum, Macdonald College, Quebec, May 13-14, 1958. Contribution No. 237 from the Goodyear Tire and Rubber Company, Research Laboratory.

TABLE I
TYPICAL CRYSTALLIZATION RATE DATA FOR TWO SAMPLES

4.5% <i>trans</i> ;	T , °C	-27.5	-30.0	-33.0	-36.5
	t_h , min	190	105	48	22
$M_c = 40,000$	T , °C	-27.5	-31.0	-33.0	-34.5
	t_h , min	130	53	33	23

coincidence, it appears that the present measurements were made at sufficiently large degrees of supercooling that the copolymers behaved as homopolymers.

The melting points of the samples were determined, a slow rate of heating being used, as outlined previously¹. The temperature at which the last measurable crystallinity disappeared was taken as the equilibrium melting point.

Typical experimental data on the control polymer have been given previously. In Table I representative experimental data on two of the modified samples are shown. Similar data were obtained on the other modified samples.

From the smoothed curve relating half-time of crystallization t_h to temperature, rates of crystallization at fixed temperatures were estimated and are listed in Tables II and III.

DISCUSSION

Gent⁸ has considered the effect of the introduction of crosslinks upon the crystallization of natural rubber and finds that the results are in agreement with an equation of the form

$$\ln(t_h)_n = \ln(t_h)_0 + nV_2/4 \quad (1)$$

where n is the concentration of points of disorder and V_2 is the volume around each crosslink prohibited to nucleation.

In Figure 1 the rates of crystallization of the isomerized samples are plotted in the form suggested by Equation (1). The results are actually expressed in terms of the relative half-times of crystallization, i.e., the half-time of crystallization of the isomerized sample divided by the half-time for the control sample at the same temperature. In Figure 1 the results for the crosslinked samples are plotted in a similar manner against $10^4/M_c$, i.e., the concentration of crosslinks.

Although Figure 1 shows the linear relationship required for Equation (1) and may be interpreted in terms of a retarding effect by the noncrystallizing units, it must be remembered that the modified samples have a depressed melting point in comparison to the starting material and consequently would be expected to crystallize more slowly at a fixed temperature. Gent⁸ has indicated that the effect of reduction in melting point is mathematically equivalent to the

TABLE II
CRYSTALLIZATION RATES OF ISOMERIZED POLYMERS

<i>trans</i> content, %	T_m °C	t_h , min, at				
		-35° C	-32° C	-28° C	-26° C	-22° C
3.6 (starting material)	-8.0	18	32	87	160	1200
4.5	-10.5	30	60	170	—	—
4.9	-12.5	52	100	300	—	—
6.9	-16.0	350	650	—	—	—
21.7	—	noncrystalline				

TABLE III
CRYSTALLIZATION RATES OF CROSSLINKED POLYMERS

M_c	$T_m, ^\circ\text{C}$	$t_{1/2}, \text{min. at}$		
		-35°C	-32°C	-28°C
Starting material	-8.0	18	32	87
(100,000)	-8.0	18	33	100
40,000	-8.5	21	40	115
15,000	-10.5	30	60	170
8,000	-12.5	53	110	—

apparent prohibition of nucleus formation by the noncrystallizing units. It is felt that an alternate and more direct way to compare the ratio of crystallization of various members of a copolymer series is to make the comparison at fixed degrees of supercooling rather than at fixed temperatures. The experimental melting points are listed in Tables II and III. The melting point-depression curves, when plotted in the usual manner, gave reasonably linear plots with heats of fusion of 400 cal/mole monomer for the isomerized samples and 200 cal/mole for the crosslinked samples. A similar melting point depression of even greater magnitude has been observed for natural rubber crosslinked with peroxide⁹. From the low values for the heat of fusion it is clear that the experimentally determined melting point depressions are greater than would be expected from theory and Flory¹⁰ has discussed the difficulties of obtaining equilibrium melting points of copolymers.

If the half-times of crystallization listed in Tables I-II are compared under similar thermodynamic conditions, i.e., in terms of the function⁶ $T_m^2/T(\Delta T)^2$, then the results shown in Figure 2 are obtained. It may be seen that all points fall near the same line except those for the 6.9% *trans* polymer. Similar results have been obtained with crosslinked natural rubber⁹. These observations have caused us to conclude that the retarded rates of crystallization of the modified polymers are directly related to the experimentally meas-

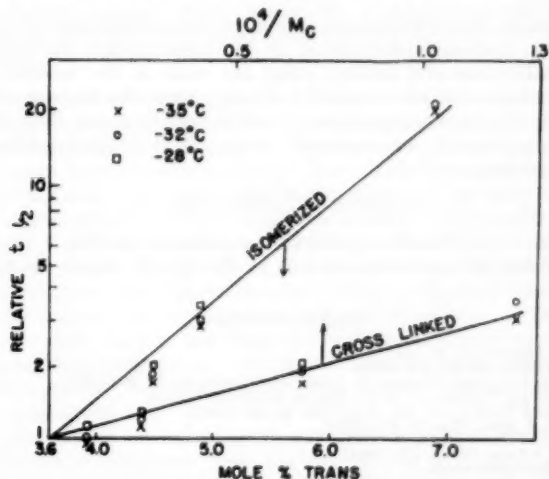


FIG. 1.—Relative half-times of crystallization at fixed temperatures as a function of concentration of noncrystallizing units.

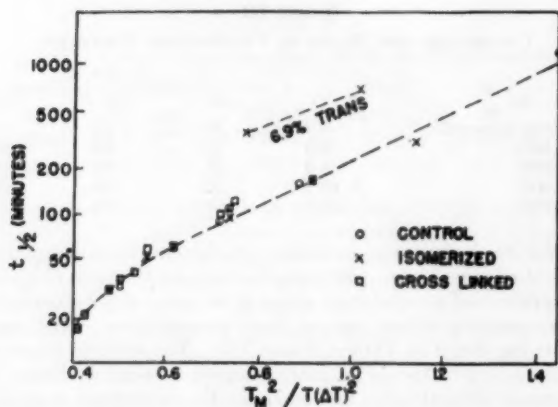


FIG. 2.—Half-times of crystallization of modified samples relative to their melting points.

ured melting point depression. Only above a critical concentration of non-crystallizing units does the retardation in rate become greater than can be accounted for by the change in melting point.

Regardless of the exact mechanism that is associated with the retarded rates of crystallization at a fixed temperature, it is evident that measurements of this type are very sensitive to changes in microstructure and in the distribution of such changes. In cases where suitable analytical techniques are lacking, crystallization measurements have proved useful in obtaining a measure of the uniformity of microstructure¹¹.

SUMMARY

From a sample of polybutadiene of high *cis*-1,4 content, the microstructure is modified by *cis-trans* isomerization or by crosslinking. Measurements of rates of crystallization and melting point are made on the modified samples. An increase in *trans* content or crosslink density markedly decreases the rate of crystallization at a fixed temperature. It is found, however, that this retardation in rate may usually be accounted for by the depressed melting point of the modified samples.

ACKNOWLEDGMENTS

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REFERENCES

- Trick, G. S., *J. Polymer Sci.* **31**, 529 (1958).
- Golub, M., *J. Polymer Sci.* **25**, 373 (1957).
- Kraus, G., Short, J. N., and Thornton, V., *Rubber and Plastics Age* **38**, 880 (1957).
- Blanchard, A. F., and Wootton, P. M., *J. Polymer Sci.* **34**, 627 (1959).
- Bekkedahl, N., and Wood, L. A., *Ind. Eng. Chem.* **33**, 381 (1941).
- Mandelkern, L., *J. Appl. Phys.* **25**, 830 (1954).
- Mandelkern, L., *SPE Journal* **15**, 63 (1959).
- Gent, A. N., *J. Polymer Sci.* **18**, 321 (1955).
- Trick, G. S., unpublished results.
- Flory, P. J., *Trans. Faraday Soc.* **51**, 848 (1955).
- Mayor, R. H., Saltman, W. M., and Pierson, R. M., *Petroleum Refiner* **37**, 208 (1958).

GENERAL CONSIDERATIONS ON THE STRUCTURE OF CRYSTALLINE HYDROCARBON POLYMERS *

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Owing to the discovery of stereospecific polymerization processes effected in our Institute, we were able to determine, in the last few years, the crystal structure of a great number of new polymers. In this work we will discuss the general principles leading to the determination of the shape and mode of packing of macromolecules in the crystals¹.

1. STEREOISOMERISM IN HEAD-TO-TAIL ALIPHATIC LINEAR POLYMERS

Before explaining the principles and discussing, in accordance with them, the crystal structure of some macromolecular compounds, we would like to emphasize the importance of stereoisomeric phenomena in the ability of the polymers to crystallize.

There are different types of stereoisomerism in organic chemistry, generally distinguished into two classes:

1) geometrical stereoisomerism, whenever the same chemical formula may correspond to intrinsically different geometrical configurations (e.g., in compounds containing a double bond, or in cyclic saturated compounds);

2) optical stereoisomerism, whenever a molecule cannot assume, by permissible rotations around single bonds, the enantiomorphous configuration (this is in most cases due to the presence of carbon atoms linked to four different substituents²).

These two cases are both important in macromolecular chemistry. Since the definition of crystal implies a three-dimensional order, in order that a polymer be crystallizable, a regularity in the succession of configurations of its monomeric units is necessarily required. A crystalline polymer can be obtained, in fact, only when all monomeric units belonging to a long chain segment show the same configuration, or when enantiomorphous configurations follow each other orderly. On the contrary, amorphous polymers are obtained when different stereoisomeric configurations of the same monomeric unit, e.g., *cis* and *trans*, or those "left" and "right" handed, follow each other disorderly. The stereospecific polymerization processes, first carried out in our Institute, permitted us to obtain head-to-tail linear polymers of alpha-olefins and di-olefins arranged according to regular successions of monomeric units, having equivalent steric configurations. These polymers are, generally, characterized by a high degree of crystallinity.

Before their discovery only a relatively limited number of crystalline synthetic hydrocarbon polymers were known. Those were obtained by poly-

* A preliminary communication on this subject was presented at the San Francisco ACS meeting, April 1958. Reprinted from *Nuovo Cimento*, Supplement No. 1 to Vol. 15, Series X, pages 9-39 (1960).

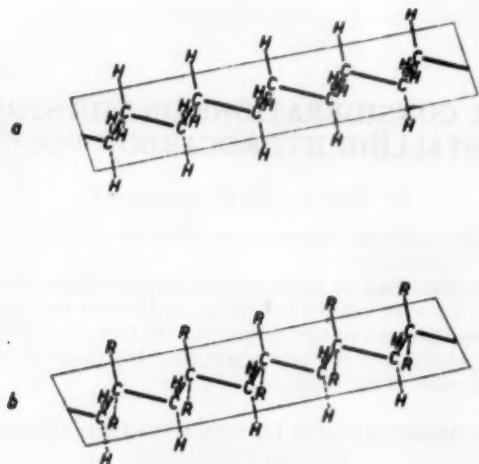


FIG. 1.—A head-to-tail succession of (a) ethylenic ($-\text{CH}_2-\text{CH}_2-$) or (b) vinylidene ($-\text{CH}_2-\text{CR}_2-$) monomer units may be realized in one way only (main chain arbitrarily stretched on a plane).

addition generally derived from monomers, such as ethylene or some vinylidene monomers containing at least two symmetry planes in their molecules (isobutylene, vinylidene chloride). When these symmetrical molecules undergo a polymerization process, only one type of head-to-tail enchainment may occur, as shown in Figure 1.

On the contrary, alpha-olefins and diolefins may give rise to various types of stereoisomeric modes of enchainment. Actually all synthetic polymers of alpha-olefins and diolefins, prepared before the discovery of stereospecific catalysis, were amorphous. Figure 2 shows molecules of stereoisomeric vinyl polymers with the chain arbitrarily settled on a plane. These are the isotactic³ polymers in which successive head-to-tail monomeric units show the same steric configuration; syndiotactic polymers⁴, in which successive head-to-tail mono-

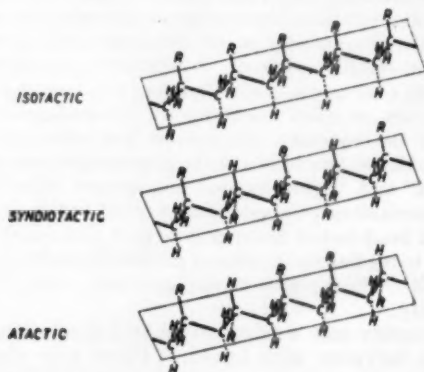


FIG. 2.—Various types of possible head-to-tail successions of vinylic ($-\text{CH}_2\text{CHR}-$) monomer units: isotactic, syndiotactic, atactic (random); (main chain arbitrarily stretched on a plane).

meric units show alternatively opposite steric configurations; atactic polymers in which successive head-to-tail monomeric units, having different configurations, are randomly distributed along the chain.

In the field of diolefin polymers other stereoisomeric phenomena of geometrical type appear. Polyisoprene regular stereoisomers with 1,4 enchainment occur in nature. Natural rubber has nearly a complete *cis* structure ($\sim 97\%$), guttapercha has a *trans* structure. Other new stereoisomers of diolefins with 1,2 enchainment, which do not exist in nature, have been synthesized in our Laboratory in the last five years.

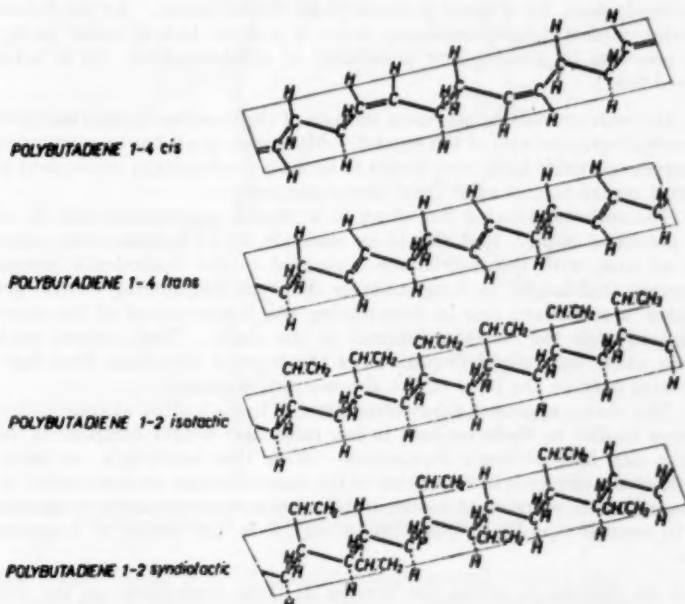


FIG. 3.—Regular successions of stereoisomer butadiene monomer units: *cis*-1,4, *trans*-1,4, isotactic 1,2, syndiotactic 1,2 (main chain arbitrarily stretched on a plane).

The configurations of the four possible regular stereoisomers of polybutadiene, whose structure was studied by us, are shown in Figure 3⁵. Stereoisomeric phenomena are practically interesting in the field of polymers, since the most interesting physical and technological properties of isotactic polymers of alpha-olefins and of some new stereoisomers of polydiolefins, in the field of plastic materials and textile fibers, are due to the ability of these polymers to crystallize⁶. Atactic polymers of alpha-olefins cannot crystallize and possess completely different properties. Their practical interest is confined to products with very high molecular weight, which give a particular type of elastomer.

The most characteristic features connected with crystallinity, such as the conformation of the chain in the crystalline state, the relative positions of the chains in the crystal, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals and so on, determine the most interesting technical characteristics of

these polymers, i.e., hardness, mechanical properties such as modulus, ultimate tensile strength and elasticity, melting temperature range, molding properties and the possibility of forming high tenacity fibers.

In this paper we shall examine the conditions necessary for the polymer to be crystallizable and the shape and mode of packing in the crystalline state.

2. SHAPE AND MODE OF PACKING OF MACROMOLECULAR CHAINS IN THE CRYSTALS

Regularity in the succession of monomeric units is the first requisite, as we have already seen, for a linear polymer to be crystallizable. As the definition of crystal implies three-dimensional order, a possible lack of order along the chain prevents in general any possibility of crystallization. It is actually observed that:

1) In linear crystalline polymers the axis of the macromolecule runs parallel to a crystallographic axis of the crystal. Moreover, in all known structures all the monomeric units have been found to occupy geometrically equivalent position with regard to this axis* (*equivalence postulate*).

2) The conformation of the chain in a crystal approaches that of minimum potential energy, that should be assumed by an *isolated* chain oriented along an axis, with the restrictions contained in the equivalence postulate. This means that lateral packing contacts (between neighboring chains) generally play a secondary role in determining the conformation of the chain in comparison with the contacts internal in the chain. Thus, lateral packing contacts cause only slight deviations of the form of the chain from the one foreseeable only on the basis of the above considerations.

3) The chains approach themselves parallel to each other at intermolecular distances similar to those realized in low molecular weight compounds, to fill possibly any hole between themselves. With this restriction, as many as possible of the elements of symmetry of the isolated chain are maintained in the lattice. That is, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions in regard to the atoms of neighboring chains.

Let us discuss, in order, the bearing of these statements on the crystal structure of polymers.

2.1 *Equivalence postulate*.—According to the equivalence postulate, all the monomeric units which form a macromolecular chain occupy equivalent positions along an axis in the crystalline state.

In turn, a condition to be fulfilled by a crystallizable polymer, is that its monomeric units have configurations, such that they may occupy equivalent positions along an axis. Let us call *isoclined* two monomeric units, whose equivalent atoms have the same z co-ordinates after a suitable translation of the origin along the chain axis z ; *anticlined*, two monomeric units whose equivalent atoms have the same z co-ordinates after a suitable translation of the origin accompanied by a reversal of direction of the z -axis.

Repetition of equivalent monomeric units may be obtained along an axis in the following ways:

1) Repetition of isoclined isomorphous equivalent units: through the operation of a translation c/p along z , accompanied by a rotation $2\pi(P/p)$ in

* This is a sufficient, but not a necessary condition, to ensure order along the chain. Because this condition appears to be most frequently verified, it may be taken as a working postulate.

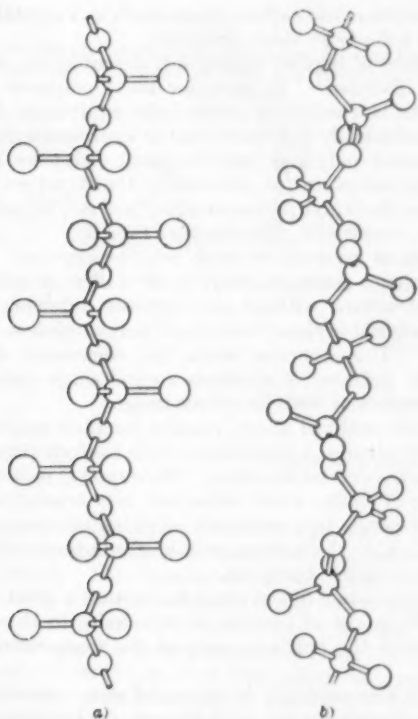


FIG. 4.—Model of the assumed structure of (left) polyvinylidene chloride (glide-plane type) as compared with the one found by A. Liguori¹⁶ for (right) polyisobutylene (helix type).

a plane perpendicular to z . A helix is thus generated which contains p monomeric units and P pitches within the period c (helix type succession).

2) Repetition of isoclined alternately enantiomorphous equivalent units: through the operation of a translation $c/2$, accompanied by a reflection in a plane containing the axis of the chain (glide-plane type succession).

3) Repetition of isomorphous alternately anticlined equivalent units: along a helix associated with twofold axes perpendicular to z .

4) Repetition of enantiomorphous anticlined equivalent units: through a translation along z associated with a symmetry plane perpendicular to z or a symmetry center.

All head-to-tail crystallizable polymers, in which the two possible chain directions are intrinsically non-equivalent (for instance, a polyamide

$$\begin{array}{c} \text{CH}_3 \\ | \\ (-\text{CH}_2)_m-\text{NH}-\text{CO}- \end{array}$$

or 1,4 polyisoprene $(-\text{CH}_2-\text{CH}=\text{C}-\text{CH}_2-)_n$) must be built up in the crystal of *isoclined* equivalent units. Hence, only the helix and the glide-plane type structures are possible. In particular, a poly-

amide containing asymmetric carbon atoms, such as a crystalline protein, must necessarily have a helix type chain structure.

All the four types of regular repetitions, described by us, are possible for vinyl head-to-tail polymers. In fact, for these polymers, the two possible chain directions can be considered intrinsically equivalent; however, we must distinguish two intrinsically different (that is stereoisomeric) types of regular successions. Isotactic polymers are the vinyl polymers able "per se" to assume a helix type structure (or, eventually, the structure type 4). Syndiotactic polymers are the vinyl polymers able "per se" to assume a glide-plane type structure (or, eventually, the structure type 3).

Other polymers, as we shall see later, may be expected, from the point of view of the equivalence postulate only, to crystallize in both the helix or the glide-plane type structure, without any intrinsic difference of stereoisomeric type (Figure 4) (polyisobutylene, helix type; polyvinylidene chloride, probably glide-plane type). This happens when the *monomeric unit* (for instance $-\text{CH}_2-\text{CR}_2-$) by permissible rotations around single bonds, may assume a conformation superposable with its mirror image.

The general rules, outlined above, require, for their practical application to the study of new structures, a knowledge of the conformation that the chain is likely to assume in the crystalline state. We should expect that the conformation of the portion of chain, which takes part in a crystalline zone, is the one which nearly corresponds to a minimum of potential energy for the molecule in free conditions (e.g. in the melting or in ideal solution) under the restrictions imposed by the equivalence postulate.

The actual conformation of the chain has in turn a great influence in determining the possible modes of packing of the chains in the crystal, and some physical properties of the polymer, such as the temperature and entropy of fusion.

2.2 Shape of the macromolecule in the crystal state.—Stable conformations of a chain should in principle satisfy, as it happens for low molecular weight compounds, the following conditions:


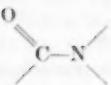

- 1) Bond length conditions⁷.
- 2) Bond angle conditions⁸.
- 3) Planarity of certain groups of atoms⁹.
- 4) Staggered carbon-carbon bonds.
- 5) As comfortable as possible Van der Waals distances between nonbonded atoms within the chain.

A compromise between these 5 conditions is generally achieved in actual structures, as we shall see later in more detail.

There is no need to illustrate the first three points: a discussion is only needed for the two last ones.

1) Principle of staggered bonds. The fourth point was emphasized first by Pitzer and coworkers¹⁰ with regard to low molecular weight hydrocarbons, such as butane. He showed, on the basis of thermodynamical calculations, that the *trans* conformation of the butane chain was more stable than the *gauche* conformation, both conformations however lying in a minimum of potential energy. *Cis* conformations of the butane chain are, on the contrary, thermodynamically unstable. C. W. Bunn was the first who applied¹¹ these ideas to the conformation of polymeric chains, and we could confirm them in a great number of cases. Because of its importance, the fourth point needs a detailed discussion.

TABLE I
SIGNIFICANT ATOMIC DISTANCES AND BOND ANGLES OBSERVED IN
POLYMERS EXAMINED IN THIS AND IN OTHER PAPERS
OF THIS SERIES

C—C	1.54 Å
C=C	1.32 Å
C—C (benzene ring)	1.40 Å
C—C—C	110° + 116°
C=C—C	120° + 125°
C—C—C (benzene ring)	120°
	all bonds in a plane
	all bonds in a plane
	all bonds in a plane

If one considers two carbon atoms C_1 and C_2 , joined by a single bond, the positions of minimum energy of the other bonds coming out from C_1 and C_2 are those outlined in Figure 5. This is probably due to repulsions between localized bonding electron pairs¹². The application of this principle alone is not sufficient to find out which conformation will be assumed by a linear saturated chain. The number of possible stable conformations is however limited by the equivalence postulate and by condition 5 of this paragraph, which implies that carbon-carbon bonds tend to be more far off than C—H bonds, favoring the *trans* conformation. Thus we arrive, for an unbranched crystallizable paraffin, at a planar zig-zag structure of the whole chain. The presence of lateral methyl or more bulky groups, may lead to a *gauche* conformation of the chain, which is the reason of the threefold helical form assumed by the molecules of isotactic polymers. Evidently comfortable accommodation of bulky lateral groups is not compatible with the maintenance of a planar zig-zag chain for isotactic polymers. As examples, in Figure 6 the structures of chain elements of polyethylene and polypropylene are shown. In Figure 7 a model of the chain of poly- α -butylene is compared with a model of the staggered structure of diamond.

If a double bond comes out from a carbon atom, it must be considered, with



FIG. 5.—Positions of minimum energy of the valence bonds of two tetrahedral singly linked carbon atoms (side and end views).

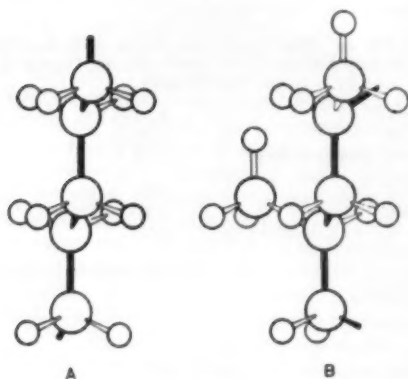


FIG. 6.—Elements of polymer chains: Polyethylene (A), Polypropylene (B).

regard to the orientating effect on the other single bonds, as lying in a plane normal to that containing the two remaining single bonds. The π -electron concentration in this perpendicular plane probably influences the direction to be assumed by the remaining bonds of successive carbon atoms. It has been indeed emphasized that the most probable distribution of electrons in a double

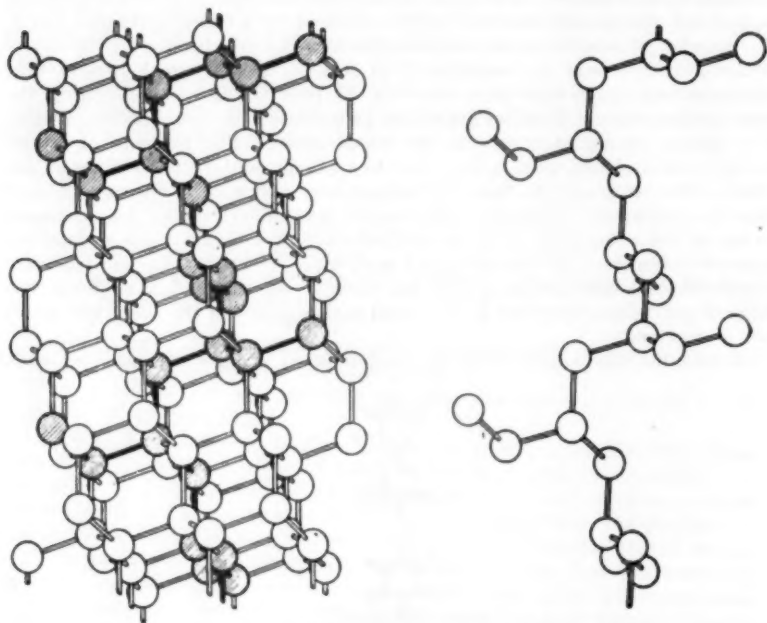


FIG. 7.—Model of the poly- α -butylene macromolecule: carbon atoms are staggered as in the diamond lattice.



Fig. 8.—Positions of minimum energy of the single bonds of a carbon atom singly linked to a double-bonded one (side and end views).

bond is the one in which two electron pairs lie on opposite sides of the plane defined by the other four bonds¹³.

The resulting effect is that the single bonds adjacent to the double bond are in staggered positions, while the double bond is not (Figure 8). As a consequence, a portion of chain containing four carbon atoms and a central double bond is planar, but the successive carbon atoms tend no longer to be in the same plane (Figure 9). This tendency explains, as we shall see later, in particular cases, the conformation assumed by the monomeric units in all four crystalline polybutadiene stereoisomers (Figure 10).

2) Van der Waals contacts. As we have already seen, Van der Waals repulsions, dealt with in the fifth point set up in this section, are extremely important in determining the form of the chains, when atoms, large in comparison with hydrogen, or lateral chains are bonded to an aliphatic chain.

Indeed, an approach of two atoms not directly bonded at a distance below the one permitted by Van der Waals forces leads to a large increase of potential energy, which opposes this approach.

Qualitatively correct Van der Waals distances between two atoms may be calculated on the basis of the additivity of Van der Waals covalent radii, when electrostatic interactions of the type involved in hydrogen bridges play no role¹⁴. Approximately, Van der Waals radii are 0.8 Å greater than the corresponding covalent radii. They cannot however be precisely defined, because only in a rough approximation atoms may be considered spherically shaped and therefore

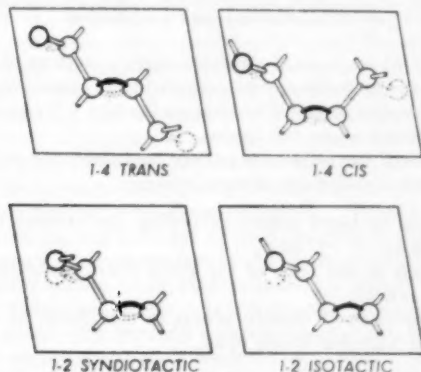


Fig. 9.—Conformation of carbon-carbon bonds adjacent to double bonds, as found in crystalline polybutadiene isomers.

much depends on the relative positions of the atoms and on the shape of the electron clouds.

The determination of the most probable shape of the macromolecule involves reconciliation of the five rules outlined above with the equivalence postulate to approach a minimum of potential energy. In many instances indeed, these five rules cannot rigorously hold together, especially when substituents of large dimensions are present along the chain. For instance, the lower heat of polymerization of isobutylene, as compared to the one of ethylene, should be

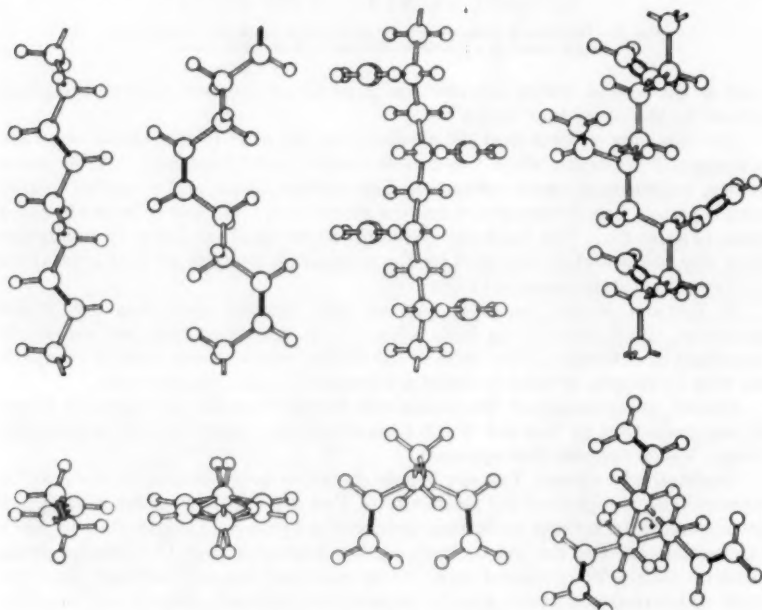


FIG. 10.—Chain conformations of the four crystalline polybutadiene stereoisomers as determined in our Institute.

attributed, partially at least, to the greater energy content of the chain C_nH_{2n} of polyisobutylene, in comparison with polyethylene, caused by the deformation of the bond sequence due to steric hindrance (as two CN_3 groups are joined to every two carbon atoms along the chain).

As a consequence of the minimum energy postulate, we may expect in some instances, while rules 1 and 3 are always holding:

- 1) A deformation of bond angles exceeding the normal values (e.g. more than 110° for $C-C-C$ angle).
- 2) A modification of the form of the main chain contrasting the principle of staggered bonds.
- 3) A greater approach of certain atoms in the chain, at distances a little below normal Van der Waals ones.

In general the above-mentioned deformations of the various types of chains take place simultaneously, but in different degrees, in order to approach a

minimum of potential energy. For the prediction of the most stable conformations, the engineering principles used in the study of elastic structure deformations should be applicable¹⁵.

Consequences of such deformations, to be discussed more deeply later, are, for instance, the non-planarity of the zig-zag chain of syndiotactic 1,2 polybutadiene, the deformation of bond angles in polypropylene, the four-fold instead of three-fold helix structure of poly-3-methylbutene.

The above outlined principles, which regard only interactions between atoms in the same chain, are of general character and should be sufficient to establish the preferred conformations of small portions of chains also in the free state.

Also, in most cases and especially for hydrocarbon polymers, they allow us to predict, together with the equivalence postulate, the conformation to be assumed by a single chain in the crystalline state. As we have already noted, however, the need of uniformly filling space may cause slight modifications in the form of the chain from the one foreseeable as that of minimum energy in the free state.

TABLE II
VAN DER WAALS CONTACTS OBSERVED IN POLYMERS EXAMINED IN THIS
AND IN OTHER PAPERS OF THIS SERIES

$\text{CH}_3\text{---CH}_3$	$4.0 \div 4.3 \text{ \AA}$
$\text{C}_{ar}\text{---C}_{ar}$ (benzene ring)	$3.5 \div 3.8 \text{ \AA}$
$\text{CH}_2\text{---CH}_2$	$4.0 \div 4.3 \text{ \AA}$
H---H	$2.4 \div 2.7 \text{ \AA}$

2.3 Mode of packing of the chains.—The order required in three dimensions of polymer chains for crystal formation may only be realized by a parallel orderly association of the chains, with contacts between atoms of different chains not exceeding the Van der Waals contacts established for low molecular weight compounds (see Table II).

When, as frequently occurs, both up and down molecules are represented in the unit cell, the space-group is such as to allow the presence in the lattice of anticlined chains in equivalent positions. When from a given monomeric unit equivalent right- and left-handed helices are likely to be built up (for example from a monomer not containing asymmetric carbon atoms, like propylene) both are often represented in the crystal lattice, and the space-group is such as to allow the presence of enantiomorphous chains in equivalent positions. It may occur, however, that when bulky side groups are present along the chain, a suitably dense packing can be obtained only in space groups in which uniquely isoclined or uniquely isomorphous helices are accommodated.

For instance, whereas in the structure of polybutylene both up and down molecules may be accommodated, only isoclined molecules are present in the closely related structure of poly-*o*-fluoro-styrene¹⁶. There is increasing evidence that in some cases, i.e., in the case of isotactic poly-*t*-butylacrylate only isomorphous helices can be accommodated in the same crystal¹⁷ so that a separation of optical antipodes occurs on crystallization from the melt, when it contains both right- and left-handed helices. In other cases, isomorphous helices provide a good filling of space only through a superspiralization, as in some proteins¹⁸.

It frequently occurs that nearly isosteric (e.g. with a similar steric encumberment) equivalent chains (e.g., enantiomorphous isoclined, or isomorphous anticlined, or enantiomorphous anticlined) may vicariate themselves in the

same lattice site. This phenomenon was observed for the first time by Nyburg in natural rubber, in the crystal lattice of which, a statistical substitution mirrored chains is possible¹⁹.

We have observed it in isotactic polymers²⁰, and found evidence for its existence also in guttapercha and polychloroprene²¹.

Generally, in the packing, the polymer molecules tend to maintain, partially at least, the symmetry of the chain. For instance, in the structure of polymers whose chains are of the glide-plane type, the glide-plane is usually maintained

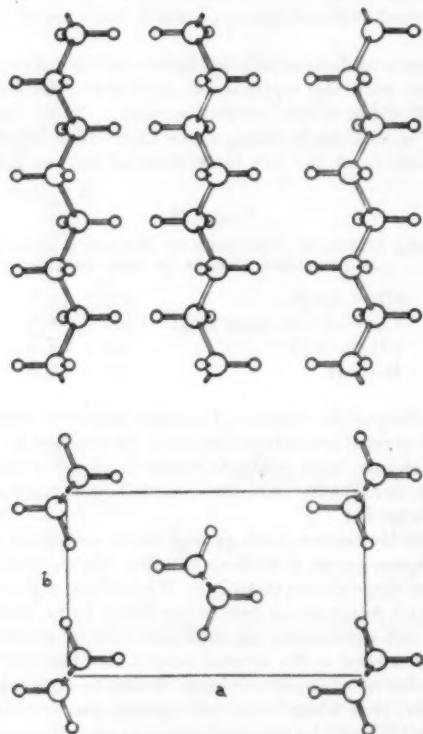


FIG. 11.—Model of the crystal structure of polymethylene.

in the lattice. This fact occurs in natural rubber, as well as in polyvinylchloride, syndiotactic 1,2 and *cis*-1,4 polybutadiene and rubber hydrochloride²². The threefold helical symmetry of the chain of poly- α -butene, polystyrene and poly-*o*-fluoro-styrene, as well as the fourfold helical symmetry of the chain of polyvinyl-naphthalene and poly-*o*-methylstyrene, are maintained in the respective crystal lattices²³.

In the parallel association of chains to provide polymer crystals, we often recognize ordered layers of macromolecules on planes by the parallel or anti-parallel association of which we may imagine that the crystal is formed. These planes are defined by the chain axis and by one of the smallest crystallographic

translations equatorial to the fiber axis. The value of both translations defining these planes are scarcely affected by thermal movements, so that thermal expansion occurs almost completely in a direction perpendicular to these planes²⁴.

We shall call them, whenever recognizable, "principal planes". They contain in general, as was mentioned above, two crystallographic axes: the fiber axis and what we call "principal equatorial axis". It is very likely that along this axis the polymer crystals may grow at their best, because generally we find it in the direction of growing of the spherulites, as we may conclude from the known structure of spherulites of polythene, polypropylene, and nylon²⁵.

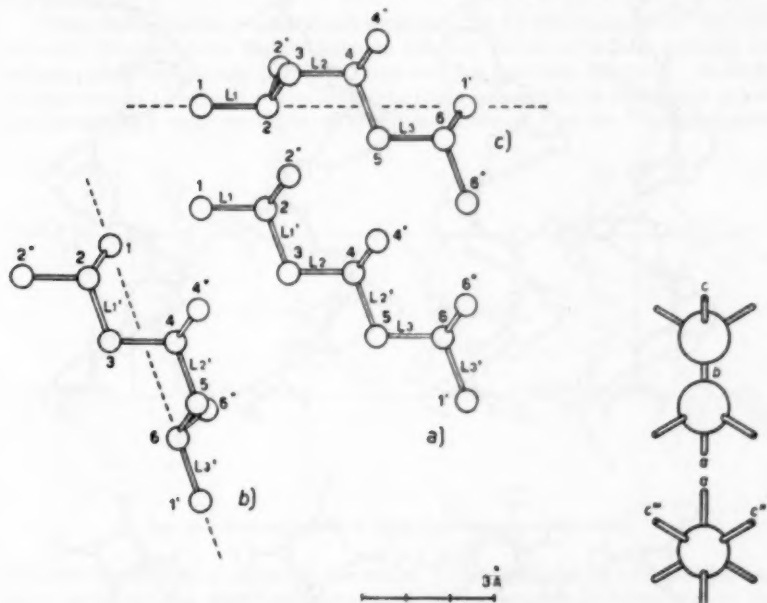


FIG. 12.—Actual conformation of isotactic polypropylene chain as derived from the planar chain structure.

With these background principles we shall now discuss in a more detailed way the structure of some crystalline polymers which have been studied by us.

3. THE STRUCTURE OF SOME CRYSTALLINE HYDROCARBON POLYMERS

3.1 Polymethylene.—Polymethylene, that is the polymer obtained by catalytic decomposition of diazomethane, is the simplest completely linear hydrocarbon polymer. Its structure is the same as that proposed by Bunn for the crystalline part of I.C.I. polyethylene²⁶. The zig-zag structure of the chain has already been discussed in this paper, in connection with the equivalence postulate and minimum energy considerations: equivalent isomorphous $-\text{CH}_2-$ groups repeat themselves along a two-fold helix. The nearly cylindrical molecules fit themselves in a quasi hexagonal array (Figure 11).

3.2 Isotactic polymers.—Isotactic polymers are the *cis* stereoisomers of the vinyl head-to-tail polymers, as we have already quoted in Section 1. The bulky dimensions of lateral groups do not allow a planar chain conformation for these polymers. A planar structure is indeed impossible, because the distance of 2.5 Å (if we consider for example polypropylene), between the nuclei of two carbon atoms of successive methyl groups is such that certain hydrogen atoms of the methyl groups would be too near to each other for minimum energy requirements²⁶. The nature of the strain may be easily understood when we consider

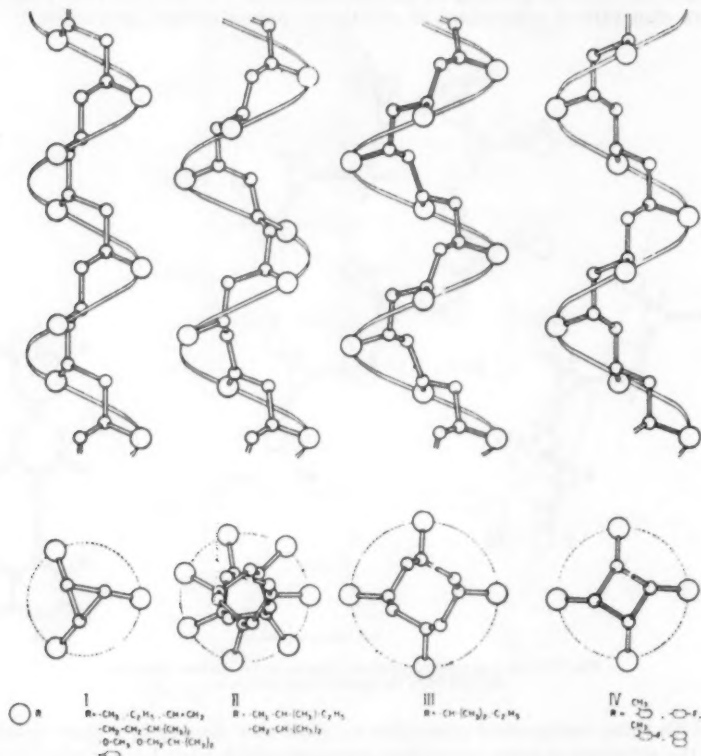


FIG. 13.—Models of helicoidal chains found for different isotactic polymers.

that the large resonance energy of polyacetylene, which has a planar structure and is crystalline, is destroyed in polypropylene, whose chain structure is nonplanar, with a net loss, according to our calculations, of about 10 kcal per monomeric unit (something like what happens with benzene and cyclooctatetraene)^{27, 28}.

A suitable accommodation of the methyl groups may be achieved in a helix type structure, imposed by the equivalence postulate, and in accordance with the principle of staggered bonds, only when the successive monomeric units are arranged on a three-fold helix.

This structure may be easily obtained from the planar one, sketched in Figure 12a), by effecting rotations of 120° around bonds, L_1, L_2, L_3 or around bonds L_1', L_2', L_3' respectively clock-wise or anticlock-wise, thus generating a left- c) or a right-handed b) helix. The methyl separation achieved in this way is comfortable ($>4 \text{ \AA}$) and the staggered bonds principle is respected. As the planar configuration is strongly unfavored from a thermodynamic point of view, no interconversion of enantiomorphous helices appears to be likely at low temperatures, and we may consider left- and right-handed helices as optical stereoisomers.

Optical activity is prevented by the presence of an equal quantity of the two forms.

When built up with normal bond lengths (1.54 \AA) and angles ($109^\circ 30'$) the isotactic threefold helix should have an identity period of 6.2 \AA ; actually for polypropylene an identity period as large as 6.5 \AA has been observed. A slight enlargement of C—C—C angles along the chain appears to be the reason of this fact, owing to a more comfortable accommodation of Van der Waals contacts

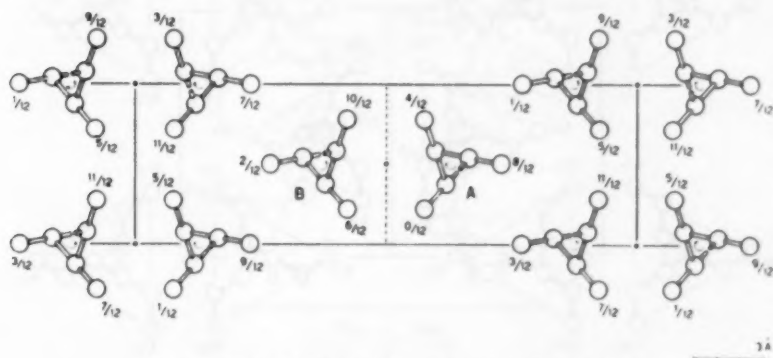


FIG. 14.—Mode of packing of polypropylene chains in the crystal.

between the hydrogen atoms of the chain. The bulkiness of side groups, and more precisely, the steric encumbrment of side groups in proximity of the chain is, on the contrary, the reason why 3-methyl substituted polyolefins have a four-fold helix structure in the crystalline state, and 4-methyl substituted ones a 3.5-fold helix structure. The staggered bonds principle is no more rigidly respected, but valence angles along the chain tend to approach the normal ones again, so that very low differences in energy should be present between a three-fold and a four-fold helix²⁰ (Figure 13).

Thus, poly- α -butene, for instance, has been observed to be crystallizable in both forms, the four-fold one however being the least stable²⁰. It has been concluded, from the fact that this form is the first which appears on crystallization both from the melt or from a solution, that in the liquid state there is a certain degree of freedom with small energy intakes, to rotation around single bonds in the chain, in the sense of a slight despiralization of the chain.

It is interesting to note that the four-fold helix poly- α -butene crystals are suddenly transformed into the three-fold helix ones by drawing or by pressing and, more slowly, on standing at room temperature.

Other different forms of chains, slightly modified from the above mentioned

ones, may also appear in crystalline isotactic polymers. For example, poly-*o*-methylstyrene has a four-fold helical chain structure, different from the one described for aliphatic polyolefins (Figure 13), whereas poly-*m*-methylstyrene has a 3.67-fold helical chain structure (11 monomeric units in three pitches along the identity period). Many complicated chain structures, which have not yet been completely examined, have been observed for other substituted polystyrenes. The reason for such a variety of different forms is to be found in the packing requirements, both within the very chain and also among different chains, the side groups of substituted polystyrenes being very stiff and bulky indeed. The solution of the complete crystal structure of polypropylene and poly- α -butene effected by us²¹ permits a discussion of the mode of packing of the chains of these isotactic polymers in crystals (Figures 14, 15).

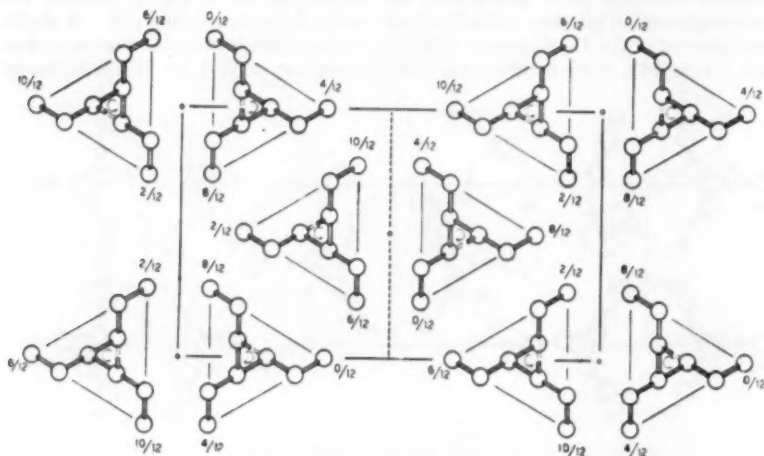


FIG. 15.—Mode of packing of poly- α -butene chains in the crystal.

On considering the packing requirements explained in Section 1, the lattice of an isotactic polymer should possibly accommodate in equal quantity enantiomorphous chains, presumably through operations of symmetry of the space group.

According to the requirements just explained, it is actually found that in all these polymers enantiomorphous chains face each other in pairs, a close packing being realized through the operation of a glide-plane with translation parallel to the fiber axis. Moreover, anticlinel isomorphous chains of the isotactic polymers of propylene and α -butene are nearly isosteric, when we refer to the encumberment of lateral groups (Figure 16) and as long as intermolecular contacts are realized almost uniquely by these lateral groups, anticlinel isomorphous chains may in principle vicariate in the same lattice site. In fact it is thought that each crystal of these polymers is composed of very small blocks of anticlinel crystallites built up of isoclinel chains, so that diffraction phenomena may be easier interpreted supposing that anticlinel isomorphous chains may statistically vicariate in each site of the crystal.

Poly- α -butene (and the closely related isotactic poly-1,2-butadiene) are able to maintain the complete symmetry of the chain, so that three glide planes

making angles of 120° among themselves and related by a three-fold screw axis are easily recognizable in the rhombohedral structure of these polymers.

A too loose mode of packing should result when a similar structure is also assumed for polypropylene.

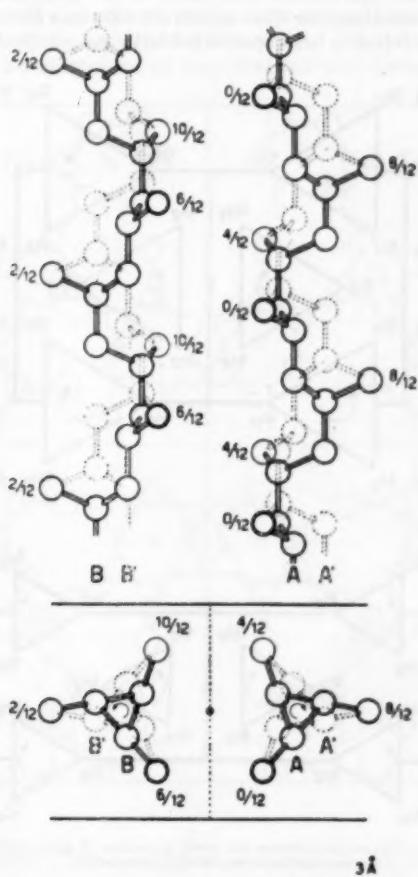


FIG. 16.—Model showing isosterism of anticlinic isomorphous chains of polypropylene in a crystal.

The glide plane, through which two enantiomorphous facing chains are related, turns out to be, in this case, a principal plane. Evidence that the a - c plane is a principal plane in polypropylene is found in the close-packing realized along this plane of the side groups of two enantiomorphous symmetrically related chains (Figure 17) and hence in the shortness of the a -axis, in its parallel orientation along the radii of spherulites and in its very low thermal expansion, as compared to the one taking place along the b -axis.

The mode of packing of four-fold helix polyvinylanthracene and poly- α -

methylstyrene is also obtained through the operation of glide-planes between enantiomorphous chains, as is seen in Figure 18.

3.3 Syndiotactic polymers.—Syndiotactic polymers may be defined as *trans* stereoisomers of the vinyl head-to-tail polymers. Their chain structure may be, according to the equivalence postulate, of the glide-plane type. Hence repetition is achieved along the fiber axis every two (*σὺν δύο*) monomeric units, or their chain may follow a helix associated with perpendicular twofold axes*.

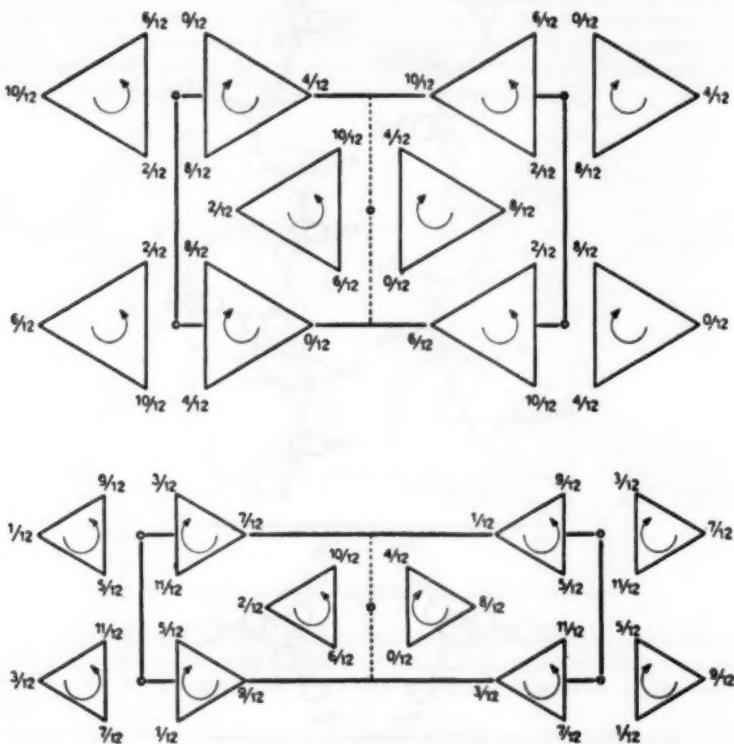


FIG. 17.—Comparison between the mode of packing of polypropylene and poly- α -butene in the crystal state.

Now it is known that two polymers possess a syndiotactic chain structure: polyvinylchloride and one of the two crystalline stereoisomers of 1,2 polybutadiene²².

The bulkiness of the side groups of these two polymers does not hinder, as was the case of isotactic polymers, a planar or nearly planar conformation of the chain. Only with regard to polybutadiene a slight deviation from a completely zig-zag planar structure of the chain has been supposed, but not thoroughly confirmed, owing to steric repulsions between successive lateral

* Note added in proof.—This is the type of chain recently found by the AA. for syndiotactic polypropylene. The model is shown in Figure 1 of the introductory paper of this series.

vinyl groups, the perpendicular orientation of which in regard to the chain axis obeys the principle of staggered bonds (Figure 19, see also Figure 9). In every case it is easy to see on inspection that no distinction is needed between up and down molecules, and in the lattice we have to accommodate only one type of chain.

The glide plane is maintained in the unit cell of these polymers. The molecules pack closely in layers along this plane. The crystal is built up of many antiparallel layers packing at their best between themselves.

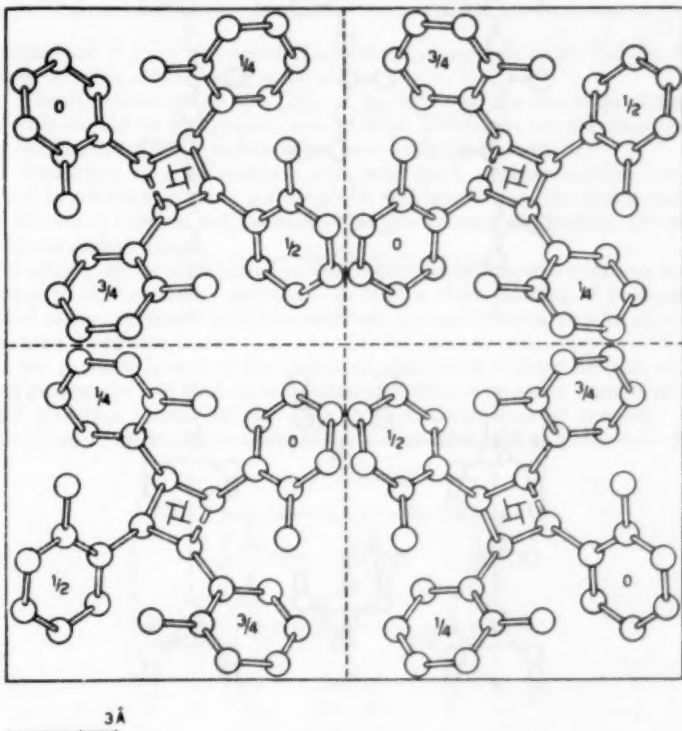


FIG. 18.—Model of packing of poly-ortho-methine cyclohexadiene in the crystal.

Thermal expansion in syndiotactic 1,2 polybutadiene occurs almost completely in a direction perpendicular to the glide-plane, according to the phenomena connected with the supposed existence of a principal plane of packing.

3.4 Crystalline 1,4 polydienes.—Under the heading of isotactic and syndiotactic polymers we have dealt with the known structure of 1,2 stereoisomeric polydienes. In this section we shall deal with the known structures of crystalline 1,4 polydienes. The synthesis of all four crystalline stereoisomers of polybutadiene and the study of their structure by the Institute of Industrial Chemistry of the Polytechnic of Milan, now permits a clearer idea of stereoisomeric phenomena in the field of polydienes.

a) *cis* 1,4 polydienes.—Natural rubber is the regular head-to-tail polymer built up of *cis*-1,4 isoprene units. Its chain structure may be expected uniquely in one of two types of successions, the glide-plane and the helix-type succession. However, it is impossible, on the basis of the equivalence postulate only, to

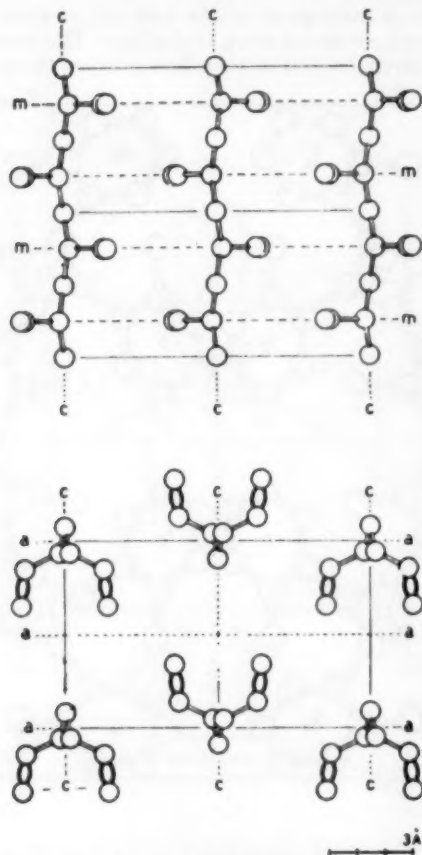


FIG. 19.—Model of packing of syndiotactic, 1,2 polybutadiene in the crystal.

establish which of the two forms will be actually chosen by the macromolecules on crystallization, as they would not correspond to intrinsic differences in the configuration of the chain.

Actually a glide-plane non-planar structure is found for the chain of crystalline *cis*-1,4 polyisoprene³². Indeed on the basis of minimum energy considerations we should expect that:

- 1) The five atoms of each monomeric unit be in a plane;
- 2) The direction of the $\text{CH}_2\text{—CH}_2$ bond should be in accordance with the principle of the staggered bonds, any of the three positions outlined in Figure 20;

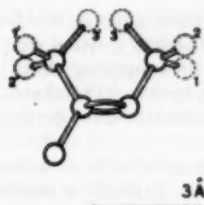


FIG. 20.—Possible conformations of *cis*-1,4 isoprene unit satisfying the principle of staggered bonds.

Positions 3 and 3' must be discarded because of excessively short Van der Waals contacts between atoms of the same chain;

3) The directions of the two $\text{CH}_2\text{—CH}_2$ bonds on the two sides of the isoprene unit should be in opposite and parallel directions; i.e. the enantiomorphous conformations 1-1' and 2-2' are best likely to be realized;

4) Repetition of a monomeric unit with such a conformation, may be achieved in a helix type or in a glide-plane type succession, the first possibility being discarded because of unsuitable contacts between the methyl group and some chain carbon atoms.

The glide-plane is maintained in the lattice, according to a common feature occurring in many studied polymers, so that a close packing of molecules is expected along this plane; also, alternatively up and down molecules should be represented along this plane.

As the contacts lateral to the principal plane thus realized are due only to methyl groups, we find that, in the actual structure, successive parallel or anti-parallel principal planes (*bc*) are able to pack themselves at random. It is possible to see from Figure 21 that a layer of molecules such as A—B—A—B can

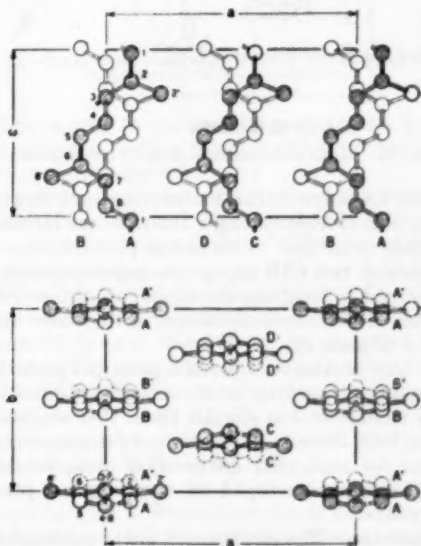


FIG. 21.—Model of the structure of *cis*-1,4 polyisoprene.

be followed equally well by a layer such as C—D—C—D or C'—D'—C'—D'.

Perhaps, we may explain the low melting entropy of rubber in comparison with the one of gutta-percha, by supposing that, in the molten state, not only a certain degree of parallelism between the chains is maintained, but also that the flexible ribbon-shaped molecules tend to maintain some kind of parallel association of the ribbons.

A great similarity of structure is to be expected between²⁴ *cis*-1,4 polybutadiene and *cis*-1,4 polyisoprene. Actually a similar conformation of the chain was found by us, in which enantiomorphous monomeric units repeat along a glide plane. No more distinction, however, is needed in *cis*-1,4 polybutadiene

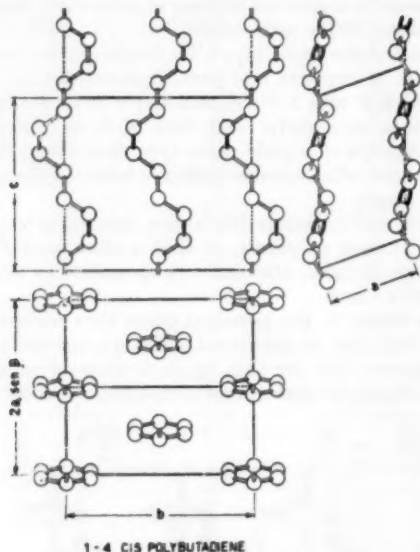


FIG. 22.—Model of the structure of *cis*-1,4 polybutadiene.

as compared with *cis*-1,4 polyisoprene between up and down molecules; also, one finds an identity period slightly longer than the one foreseeable on the basis of the staggered bonds principle. This fact is probably due to repulsions between hydrogen atoms of two CH₂ groups, in opposite position relative to the double bond, which tend to lengthen the chain; repulsions which could not be eliminated in the case of polyisoprene because of the steric hindrance provided by the methyl group (Figure 22).

The glide-plane may be also considered a principal plane in polybutadiene, and determines a mode of packing of the macromolecules in the crystalline state, which is very similar to, but simpler than, that realized in the structure of polyisoprene. In fact, there is no more need for accommodation of up and down molecules, nor for statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane, owing to the absence of lateral groups.

b) *trans* 1,4 polydienes.—The structure of gutta-percha, the *trans*-1,4 head-to-tail stereoisomer of polyisoprene, was thoroughly studied for the first time

by C. W. Bunn³⁵, who assessed the principal features of the structure of one of the three crystalline forms in which this polymer may occur (β form).

Some strangeness of the chain structure was eliminated by Jeffrey³⁶, supposing and proving that the five atoms of each isoprene unit must be in a plane.

As a matter of fact, successive *trans* isoprene units may repeat according to the principle of the staggered bonds in various ways without any great difference in regard to sterical hindrances and, according to this fact, different identity periods have been found for the three different crystalline forms in which guttapercha may occur. However, there is no complete agreement as to the form of the chains, reported from different authors.

In accordance with the equivalence and minimum energy postulate we tentatively proposed the three forms shown in Figure 23, whose calculated identity periods are in accordance with literature data³⁷.

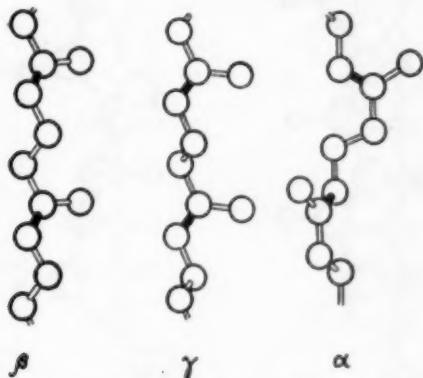


FIG. 23.—Model of the chain of guttapercha (*trans*-1,4 polyisoprene) in different crystalline modifications.

A chain structure similar to the one of β -guttapercha is possessed by *trans*-1,4 polybutadiene, which according to our studies can also appear in different crystal forms as does guttapercha³⁸.

This polymer shows in its crystal state at room temperature a chain structure (with an identity period $c = 4.92$) very similar to that of β -guttapercha (Figure 24). The almost cylindrical shape of its molecules favors a mode of chain packing in a pseudo-hexagonal array with $a = 4.54$ Å. At about 65° C a first order transition in the solid state takes place. The structure of the high temperature phase corresponds to a mode of packing in which the chains, always remaining parallel to each other, should be more free to move and rotate along the chain axes. The phase change is accompanied by a lowering of the density of more than 9%. The low density phase possesses a pseudo-hexagonal array with $a = 4.88$ Å, $c = 4.68$ Å. In a drawn fiber this transformation gives rise to a sudden reversible contractile process, which is obviously analogous to the one taking place in living muscles.

The dimensional change along the fiber axis corresponds to the change of the c dimension (about 5%). We believe this is the first time that a similar phenomenon has been observed in synthetic fibers, related to a first order crystal-crystal transition.

4. OTHER NOTABLE STRUCTURES

The principles discussed in this work with regard to hydrocarbons may be also applied to other notable structures of non-hydrocarbon polymers; so we report some examples to demonstrate the general validity of the principles previously discussed.



FIG. 24.—Model of the chain of *trans*-1,4 polybutadiene.

Nylons.—The form of the chain of nylon is found to be nearly planar in accordance with the principle of staggered bonds³⁹. Hydrogen bonds are formed among different molecules in the same plane in which the chain is contained; successively these planes pack themselves at their best. Along these planes the direction of accretion of spherulites is found.

At the melting point⁴¹ we should expect disruption of the lattice prevailing in a direction normal to this plane. As long as thermal oscillations should occur at their best, owing to lower potential barriers, around $\text{CH}_2\text{—CO—}$ and NH—CH_2 bonds, giving rise to typically different deviations from the planar

form of the chain, a lower packing efficiency and then a lower melting point should be expected for nylon 6 in comparison with nylon 66 (Figure 25) and, more generally, for nylons containing odd sequences of CH_2 groups in comparison with those containing even sequences of CH_2 groups.

There is some evidence that a slight deviation from the completely planar form is present in nylon 66 and nylon 6 even at room temperature. The fact which has not yet been explained that nylons have a lower heat and entropy of fusion than polyolefins or polyethers supports our assumption that hydrogen bonds are statistically maintained on layers also in the melt.

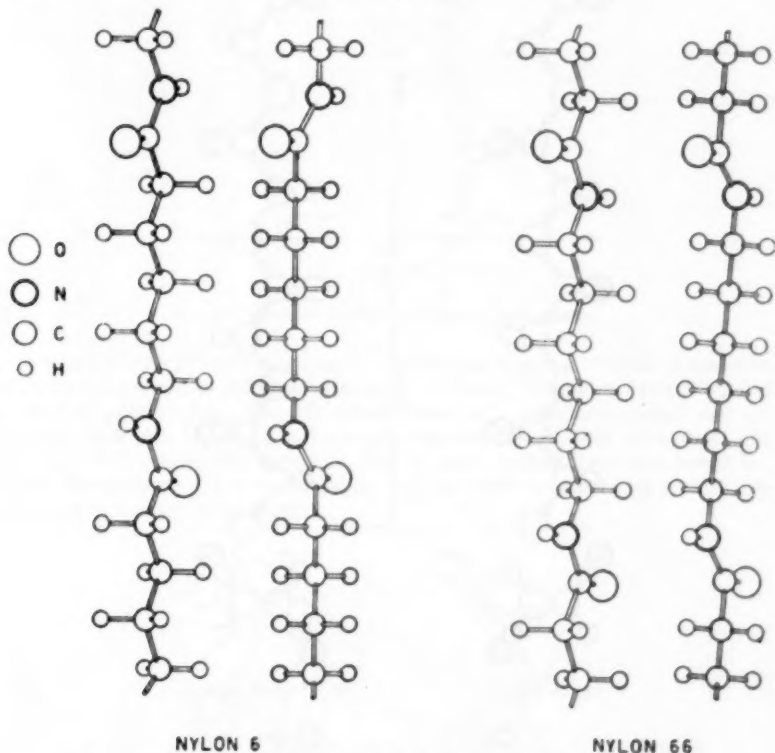


FIG. 25.—Possible models of the chains of nylon 6 and nylon 66 slightly deviating from planarity in a thermal vibration.

Teflon.—Teflon is the polymer of tetrafluoroethylene. According to the principle of staggered bonds the best form of the chain should be the planar one; but, owing to repulsions between fluorine atoms, a slight spiralization of the chain occurs, giving rise to a helix along a pitch of which 13 CF_2 units repeat themselves⁴¹.

The chains have an almost cylindrical encumberment, so that they pack in a pseudo-hexagonal array.

Polyisobutene⁴², polyvinylidene chloride⁴³.—The complete crystal structures of these polymers are not known; but the form of their chains is supposed to be

of the glide-plane type for polyvinylidene chloride, and, according to Liquori, of the helix-type for polyisobutene as may be deduced from the length of the fiber axis and the principal features of their x-ray spectra. The deviation from staggered structures of their chain is certainly due to the great steric encumbrance of the lateral groups (see Figure 4).

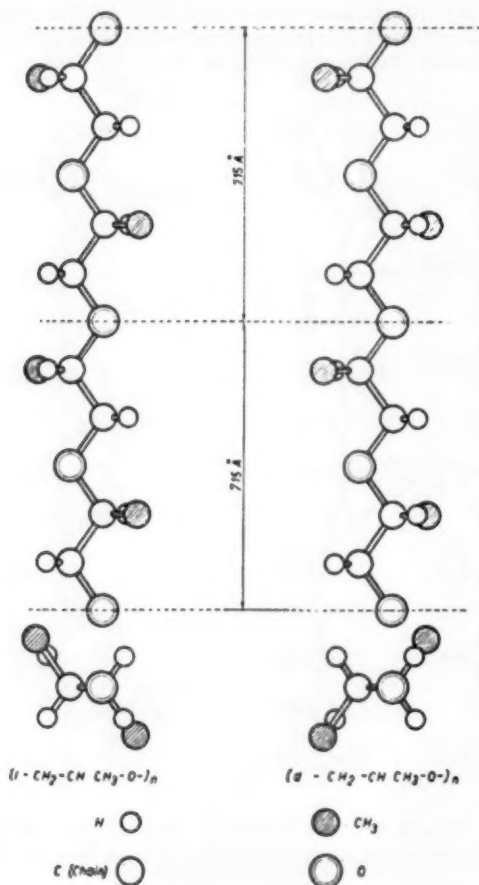


FIG. 26.—Model of the chain of d- and l-polypropylene oxide.

Polypropylene-oxide⁴⁴.—This polymer has been studied by us, and it is of some interest because the monomer contains asymmetric carbon atoms. In fact a helix structure has been found, in accordance with the equivalence postulate, satisfying the minimum energy requirements. When prepared from the racemic monomer, a crystalline polymer is obtained only with stereospecific catalysts, which permit the growing of chains only from isomorphous monomeric units (Figure 26).

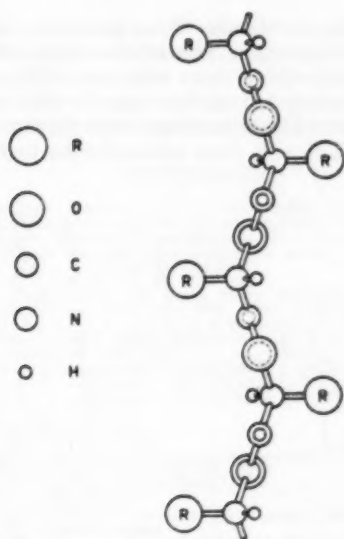


FIG. 27.—Model of the chain of β Keratin type proteins.

*Polyvinylalcohol*¹⁵.—This polymer, notwithstanding the irregular succession of hydroxyl groups, is able to crystallize. Actually, the chain form is similar to that of polyethylene, the OH groups being of a sufficiently small size (in comparison to the H atoms) to be accommodated also in a *cis* succession. In the crystal structure, the molecules face in pairs, having hydrogen bonds between themselves, whenever possible, i.e., at random, according to the distribution of the hydroxyl groups.

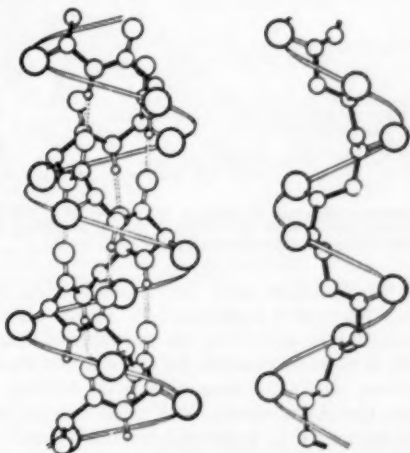


FIG. 28.—Model of the chain of α Keratin type proteins (left), compared with the chain of a 3.5 helix isotactic polymer (right).

*Proteins*⁴⁶.—According to whether hydrogen bonds are formed between different chains or in the same chain, two different kinds of helix type structures are possible for the chain: 2-fold helix structures (Figure 27) (the packing being determined by hydrogen bonds on opposite sides of the chain along a principal plane) or more-fold helix structures with the plane of the amide group parallel to the chain axis so as to form intramolecular hydrogen bonds (Figure 28) within the chain.

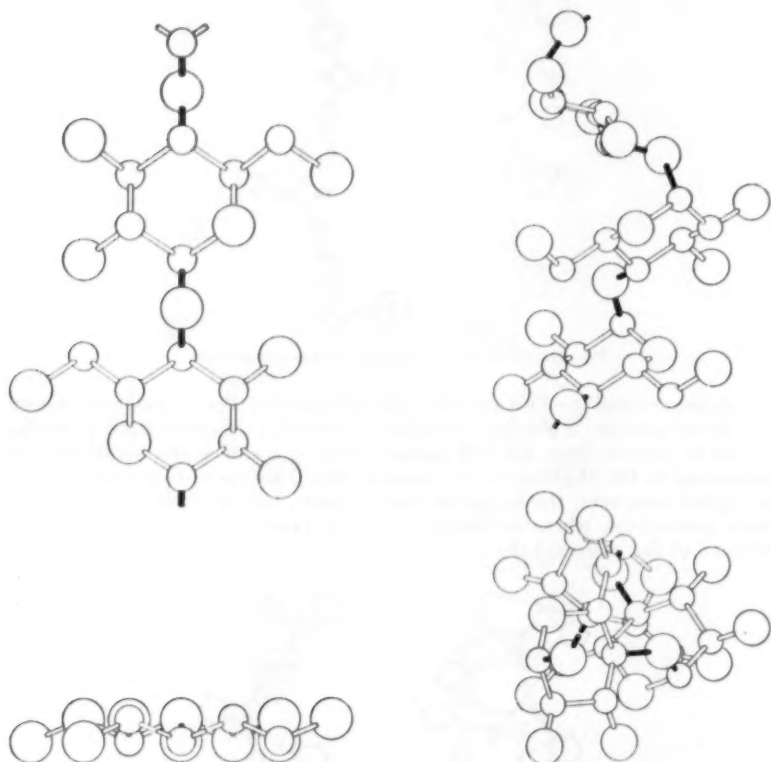


FIG. 29.—Comparison between the chain of cellulose (left) and that of starch (right). The piranic ring is rigid. The black drawn bonds, joining the rigid rings through an ethereal oxygen atom, follow one to another like polymethylene (cellulose) and polypropylene (starch) bonds.

Polysaccharides^{47, 48}.—Cellulose may be considered as the 1,4 connected polymer of α -glucose. Successive α -glucose residues are able to follow a 2-fold helicoidal path, without strain, satisfying the principle of staggered bonds.

A 2-fold helix path is no more possible for the chain of starch, which is built up of β -glucose residues, so that a three-fold helix results. Close similarity may be found between the chain structures of these two polymers, respectively with the 2-fold helix structure of polyethylene (all "trans" bonds) and with the 3-fold helix structure of polypropylene (alternatively "trans" and "gauche" bonds) (Figure 29).

The packing of the chains of polysaccharides appears mostly dependent on the formation of strong intermolecular hydrogen bonds.

The uniqueness of helix-type structures for the chain of crystalline proteins and polysaccharides follows directly from the equivalence postulate, as the corresponding monomeric units contain asymmetric carbon atoms.

REFERENCES

- ¹ Natta, G., *Atti Acc. Naz. Lincei, Memorie* **4** (8), 61 (1955); Natta, G. and Corradini, P., *Atti Acc. Naz. Lincei* **4** (8), 73 (1955); Natta, G., *J. Polymer Sci.* **16**, 143 (1955); Natta, G., Pino, P., Corradini, P., Danusso, F., Mantica, E., Mazzanti, G., and Moraglio, G., *J. Am. Chem. Soc.* **77**, 1708 (1955).
- ² Todd, A., *Perspectives in Organic Chemistry* (New York, 1956), p. 68.
- ³ Natta, G., *Atti Acc. Naz. Lincei, Memorie* **4** (8), 61 (1955).
- ⁴ Natta, G. and Corradini, P., *J. Polymer Sci.* **20**, 251 (1956).
- ⁵ Natta, G. and Corradini, P., *Rend. Acc. Naz. Lincei*, **19** (8), 229 (1955); Natta, G., Corradini, P., and Porri, L., *Rend. Acc. Naz. Lincei* **20** (8), 728 (1956); Natta, G. and Corradini, P., *Angew. Chemie* **68**, 615 (1956); Natta, G., Corradini, P., and Bassi, I. W., *Rend. Acc. Naz. Lincei* **23** (8), 363 (1957).
- ⁶ Natta, G., *Rubber and Plastic Age* **38**, 6 (1957); *Esperientia*, suppl. **6**, 21 (1957); *Materie plastice* (1958), p. 1; *Chemistry and Industry* **47**, 1520 (1957).
- ⁷ Stuart, H. A., *Die Physik der Hochpolymeren* **1** (Berlin, 1952), p. 160.
- ⁸ Stuart, H. A., *Die Physik der Hochpolymeren* **1** (Berlin, 1952), p. 172.
- ⁹ Stuart, H. A., *Die Physik der Hochpolymeren* **1** (Berlin, 1952), pp. 17 and 21; Giacomello, G. and Corradini, P., *Ric. Scient.* **22**, 41 (1952).
- ¹⁰ Pitzer, K. S., *J. Chem. Phys.* **5**, 473 (1937).
- ¹¹ Bunn, C. W., *Proc. Roy. Soc. A* **180**, 67 (1942).
- ¹² Mizushima, S. I., *Structure of Molecules and Internal Rotation* (New York, 1954).
- ¹³ Gillespie, R. J. and Nyholm, R. S., *Quart. Rev.* **11**, 339 (1957).
- ¹⁴ Stuart, H. A., *Die Physik der Hochpolymeren* **1** (Berlin, 1952), p. 97.
- ¹⁵ Pegoraro, M., *Lingonere* **32**, 965 (1958).
- ¹⁶ Natta, G., Corradini, P., and Bassi, I. W., *Suppl. Nuovo Cimento* **15**, 83 (1960).
- ¹⁷ Natta, G. and Corradini, P., unpublished data.
- ¹⁸ Pauling, L. and Corey, R. B., *Nature*, London, **171**, 59 (1953).
- ¹⁹ Nyburg, S. C., *Acta Cryst.* **7**, 385 (1954).
- ²⁰ Natta, G., Corradini, P., and Bassi, I. W., *Suppl. Nuovo Cimento* **15**, 68 (1960).
- ²¹ Corradini, P., and Cesari, M., unpublished data.
- ²² Natta, G. and Corradini, P., *Rend. Acc. Naz. Lincei* **19** (8), 229 (1955); *J. Polymer Sci.* **20**, 251 (1956); Nyburg, S. C., *Acta Cryst.* **7**, 385 (1954); Natta, G. and Corradini, P., *Suppl. Nuovo Cimento* **15**, 111 (1960); Bunn, C. W. and Garner, E. V., *J. Chem. Soc.* 654 (1942).
- ²³ Corradini, P., and Ganis, P., *Suppl. Nuovo Cimento* **15**, 96, 104 (1960).
- ²⁴ Corradini, P., work presented at the National Congress of Chemistry (Turin, 1958), see *Angew. Chemie* **70**, 598 (1958).
- ²⁵ Keller, A., *J. Polymer Sci.* **15**, 31 (1955); **21**, 363 (1956).
- ²⁶ Bunn, C. W., *Trans. Far. Soc.* **35**, 482 (1939).
- ²⁷ Natta, G., Lecture held at the Summer Course of Varenna (1956), *Ric. Scient.*, in press.
- ²⁸ Corradini, P., *Rend. Acc. Naz. Lincei*, in press.
- ²⁹ Corradini, P., and Pasquon, I., *Rend. Acc. Naz. Lincei* **19** (8), 453 (1955).
- ³⁰ Natta, G., Corradini, P., and Bassi, I. W., *Rend. Acc. Naz. Lincei* **19** (8), 404 (1955).
- ³¹ Natta, G. and Corradini, P., *Suppl. Nuovo Cimento* **15**, 40 (1960); Natta, G., Corradini, P., and Bassi, I. W., *Suppl. Nuovo Cimento* **19**, 52 (1960).
- ³² Natta, G. and Corradini, P., *J. Polymer Sci.* **20**, 251 (1956).
- ³³ Nyburg, S. C., *Acta Cryst.* **7**, 385 (1954); Natta, G. and Corradini, P., *Angew. Chemie* **68**, 615 (1956).
- ³⁴ Natta, G. and Corradini, P., *Suppl. Nuovo Cimento* **15**, 111 (1960).
- ³⁵ Bunn, C. W., *Proc. Roy. Soc. A* **180**, 40, 82 (1942).
- ³⁶ Jeffrey, G. A., *Trans. Far. Soc.* **40**, 517 (1944).
- ³⁷ Natta, G., Corradini, P., and Porri, L., *Atti Acc. Naz. Lincei* **20** (6), 728 (1956).
- ³⁸ Natta, G., Corradini, P., Porri, L. and Morero, D., *Chimica e Ind.* **40**, 362 (1958).
- ³⁹ Bunn, C. W., and Garner, E. V., *Proc. Roy. Soc. London*, **A189**, 39 (1947); Holmes, D. R., Bunn, C. W., and Smith, D. J., *J. Polymer Sci.* **17**, 159 (1955).
- ⁴⁰ Corradini, P., *Ist. Lomb. Scienze e Lettere* **91**, 884 (1957).
- ⁴¹ Bunn, C. W., and Howells, E. R., *Nature* **175**, 549 (1954).
- ⁴² Liquori, A. M., *Acta Cryst.* **8**, 345 (1955).
- ⁴³ Fuller, C. S., *Chem. Rev.* **26**, 143 (1940).
- ⁴⁴ Natta, G., Corradini, P., and Dall'Asta, G., *Rend. Acc. Naz. Lincei* **20** (8), 408 (1956).
- ⁴⁵ Bunn, C. W., *Nature* **161**, 929 (1948).
- ⁴⁶ Pauling, L., and Corey, R. B., *Proc. Nat. Acad. Sci.* **37**, 205-282 (1951).
- ⁴⁷ Meyer, K. H., and Mich, L., *Helv. Chim. Acta* **20**, 232 (1937).
- ⁴⁸ Kreger, D. R., *Biochem. Biophys. Acta* **6**, 406 (1951).

THE CRYSTAL STRUCTURE OF *CIS*-1,4 POLYBUTADIENE *

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In previous works¹, we announced the identification and discussed the structure of three of the four possible pure stereoisomers of polybutadiene; two with 1,2 enchainment (isotactic and syndiotactic respectively) and the third with *trans*-1,4 enchainment.

In a letter to the Editor of *Angewandte Chemie* we have given preliminary data concerning the crystal structure of the polymer with *cis*-1,4 configuration, of which we succeeded in preparing sufficiently long and crystallizable macromolecular chains formed by *cis*-1,4 units².

All the various stereoisomeric polymers we examined were prepared with different catalysts, all obtained by reaction of metalalkyls on suitable compounds of transition elements³.

For all these catalysts the mechanism of the polymerization reaction is of the co-ordinated anionic type. The different behavior can be ascribed to the mode of co-ordination of the olefin with the metallorganic complex of the transition metal.

As is well known, polybutadienes, previously prepared by methods of radical or cationic polymerization type, have always given amorphous products and when examined by infrared methods show the presence of monomeric units having 1,2 enchainment together with monomeric units having 1,4 enchainment and *cis* and *trans*-1,4 configurations, irregularly distributed along the polymeric chain. At first the preparation of polybutadiene having very high *cis*-1,4 content was obtained by fractionating a mixture of macromolecules with 1,4 enchainment and different steric composition⁴. Following this method it was possible to obtain fractions having a melting point almost of 0° C, consisting of macromolecules showing a *cis*-1,4 configuration for very long sections of their chains, at least. In fact, the melting point of these fractions is practically the same as that observed in polymers successively prepared with other highly stereospecific catalysts, which give crude products having a content in *cis*-1,4 units greater than 98%. The melting point of practically pure (>99% *cis*-1,4 units), unstretched, polybutadienes prepared in this Institute is +1° C⁵.

In this note we will only report the data which we have obtained on the structures of *cis*-1,4 polybutadiene, which differs from the other pure stereoisomeric butadiene polymers in that it has a greater similarity to natural rubber because it possesses highly reversible elasticity with low hysteresis and crystallizes under stretch at room temperature and even at higher temperatures.

In Table I, for example, we give some mechanical properties of our polymer which are very similar to those obtainable for natural rubber.

* Reprinted from *Nuovo Cimento*, Supplement No. 1 to Vol. 15, Series X, pages 111 to 121 (1960).

TABLE I
PHYSICAL PROPERTIES OF VULCANIZED POLYBUTADIENES WITH A HIGH
CONTENT IN *cis*-1,4 STEREOISOMER (PURE GUM RECIPE)

<i>cis</i> -1,4 content	92-93%	98-99%
Mooney viscosity, ML 4	90-95	70-80
Tensile stress (psi)	800-1100	2500-2800
Elongation at break, %	900-1000	850-950
Modulus at 300% elongation (psi)	140-180	140-180
Resilience at 20° C, %	80-85	85-88
Hardness, Shore A	45-50	45-50
Compounding recipe:		
Polybutadiene		100
Stearic acid		2
Zinc oxide		3
Sulfur		1
Vulcafor MBTS (di-2-benzothiazyl disulphide)		1.3
Nonox D (phenyl-2-naphthylamine)		1
Cure: 145° C × 45 min		

1. ROENTGENOGRAPHIC DATA

The *cis*-1,4 polybutadiene has a melting point of about +1° C but, as was stated above, it may exist in the crystalline state under stretching at room temperature and even at higher temperatures.

The x-ray spectra of the polymer were obtained, in a cylindrical camera, on samples stretched at (300 ÷ 400)% and cooled at about -30° C with a jet of carbon dioxide from dry ice, in order to have reflections as sharp as possible.

The samples examined have fiber photographs very rich in reflections which denote a high degree of order both for equatorial and longitudinal directions (Figure 1).

The establishment of the unit cell was effected by the standard methods of the reciprocal lattice⁶.

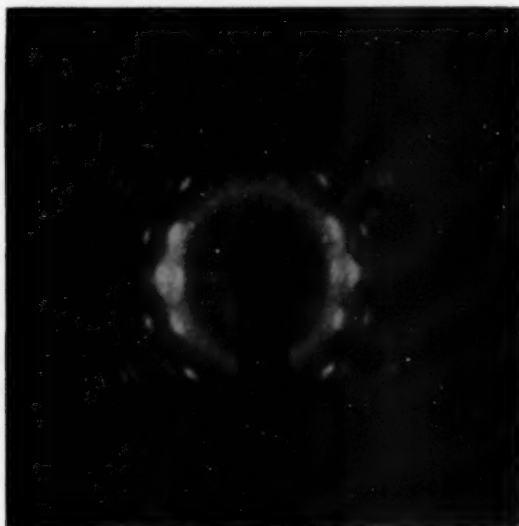


FIG. 1.—Fiber spectrum of *cis*-1,4 polybutadiene.

The unit cell appeared monoclinic; its constants are $a = 4.60 \text{ \AA}$, $b = 9.50 \text{ \AA}$, $c = 8.60 \text{ \AA}$ (fiber axis). The axis c is inclined on the axis a ; the angle between the axes results $\beta = 109^\circ$ (all data within about 1% accuracy).

The calculated density, assuming that four monomeric units are contained in the unit cell, is 1.01, in accordance with the experimental value.

The most characteristic extinction, which becomes evident from the reciprocal lattice description, is that of hkl reflections with $h + k = 2n + 1$. This extinction is common to five monoclinic space groups⁷, say, C_s^2 , C_s^4 , C_2^2 , C_{2h}^2 , C_{2h}^3 .

Some of these space groups are characterized by further extinctions, as reported below:

$$\begin{array}{l} C_s^2 \text{ none; } C_s^4 \quad h0l \text{ if } l = 2n + 1; \quad C_2^2 \text{ none} \\ C_{2h}^2 \text{ none; } C_{2h}^3 \quad h0l \text{ if } l = 2n + 1 \end{array}$$

Actually, it was not possible to observe any reflection $h0l$ with $l = 2n + 1$; then we found it advisable to retain C_s^4 and C_{2h}^3 as the most probable space groups.

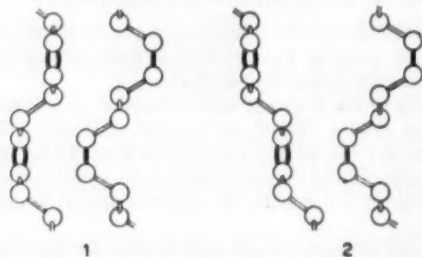


Fig. 2.—Possible conformations of a succession of 1,4 *cis* polybutadiene monomeric units satisfying the principle of staggered bonds.

As is well known, the unequivocal establishment of the space group of the unitcell of a polymer must be generally delayed, until reasonable considerations relative to the symmetry of the macromolecules and to their mode of packing may be made. Two different conformations are possible for the monomeric unit on the basis of the principle of staggered simple bonds⁸ which we have discussed in previous works. They are schematically illustrated in Figure 2, where we have shown for each of them two projections, normal to the chain axis.

In natural rubber, the conformation 2 is actually present in the crystalline state⁹.

In our case the period calculated for the conformation 2 with normal distances and angles (8.4 \AA) is in much better agreement with the period we found experimentally (8.6 \AA) than with the period calculated for the conformation 1 (8.1 \AA).

In the type 2 conformation the arrangement of the monomeric units gives rise to a glide plane type chain, which satisfies the principles of staggered bonds and the minimum energy postulate⁸. The chain contains symmetry centers and, as said above, a glide plane with translation. These symmetry elements are contained all together in the space group C_{2h}^3 . These considerations brought us to effect the study of the structure models corresponding to this space group and to compare the experimental and calculated intensities, in order to reach a confirmation of the space group. On the basis of this assumption, since two

TABLE II
CO-ORDINATES OF THE INDEPENDENT STRUCTURAL UNITS OF
POLYBUTADIENE

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
CH ₂	0.112	0.000	0.088
CH	0.046	0.127	0.183

chains in 0 0 0 and $\frac{1}{2} \frac{1}{2} 0$ must be contained in the cell, the positions of only two carbon atoms are enough for describing the whole structure.

A very good agreement between experimental and calculated intensities (Table III) was obtained assuming the co-ordinates given in Table II.

In Figure 3 the resulting mode of packing is shown.

As may be seen, it is particularly simple and allows a homogeneous filling of the space. The contact distances between carbon atoms of neighboring molecules are all greater than 3.8 Å, in good accordance with the results obtained examining other known structures. The Fourier projection of the electron density on (0 0 1) is shown in Figure 4.

2. COMPARISON OF THE CHAIN STRUCTURES OF THE DIFFERENT STEREOISOMERIC POLYBUTADIENES

By the synthesis of *cis*-1,4 polybutadiene and the determination of its structure the study of the series of the pure stereoisomers of polybutadiene was completed; we think it is interesting, therefore, to compare the different structures we found. The case of 1,2 polymerization is analogous to the one of

TABLE III
COMPARISON BETWEEN THE OBSERVED AND CALCULATED
STRUCTURE FACTORS (*B* = 5.7 Å²)

<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>
0 2 0	32	37	2 4 1	<1	—
1 1 0	42	45	3 1 1	2	—
1 3 0	1	—	3 3 1	1	—
0 4 0	—	—	3 1 1	4	—
2 0 0	15	16	2 6 1	5	7
2 2 0	2	—	1 7 1		
1 5 0	1	—	1 1 2	16	21
2 4 0	6	—	0 2 2	11	13
0 6 0	10	12	1 1 2	16	18
3 1 0	<1	—	1 3 2	21	23
3 3 0	6	—	2 0 2	12	12
1 7 0	9	9	2 2 2	25	19
2 6 0	1	—	0 4 2		
0 8 0	10	12	1 3 2		
3 5 0	4	—	2 0 2	19	18
1 1 1	32	35	1 5 2	12	13
0 2 1			2 4 2	13	10
1 1 1			2 2 2		
1 3 1	10	8	1 5 2	3	—
1 3 1	11	10	3 1 2	5	—
0 4 1	1	—	0 6 2	3	—
2 2 1	8	8	2 4 2	1	—
2 2 1	11	10	3 3 2	3	—
1 5 1	6	7	2 6 2	6	—
1 5 1	7	7	1 7 2	4	—
2 4 1	<1	—	3 1 2	10	9
0 6 1	8	9	0 0 2	6	6

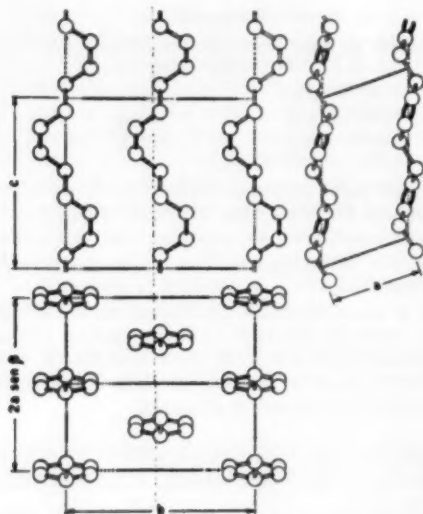


FIG. 3.—Model of the structure of *cis*-1,4 polybutadiene.

vinyl polymers. The only two possibilities of forming a crystallizable polymer having a regular and simple structure are those of having an isotactic polymer (for which a threefold screw chain conformation was expected and has been actually found) or a syndiotactic polymer (for which the structural equivalence of the monomeric units is realized by the presence of a glide plane with translation along the fiber axis¹).

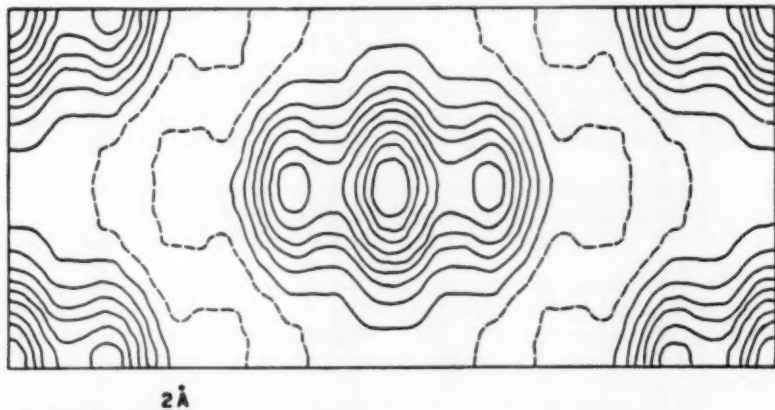


FIG. 4.—Projection of the electron density on (001) (contours are drawn at $1e/\text{\AA}^2$, the dashed line represents the $1e/\text{\AA}^2$ level).

Whereas the polymerization occurs with the formation of chains having 1,4 enchainment, one of the two possible pure stereoisomers (which have also been studied by us) is with regular *cis*-1,4 enchainment, and the other with regular *trans*-1,4 enchainment. It is interesting to note how, in their pure state, both polymers having 1,2 enchainment and the one having *trans* 1,4 enchainment do not show elastomeric characteristics at room temperature, but, on the contrary, they show features of crystalline products, able to be oriented by mechanical treatments and, therefore, to form fibers. These features which were not foreseen for a polymer of butadiene, may be easily understood because of the high crystallinity at room temperature, the high molecular weight and the high melting temperature.

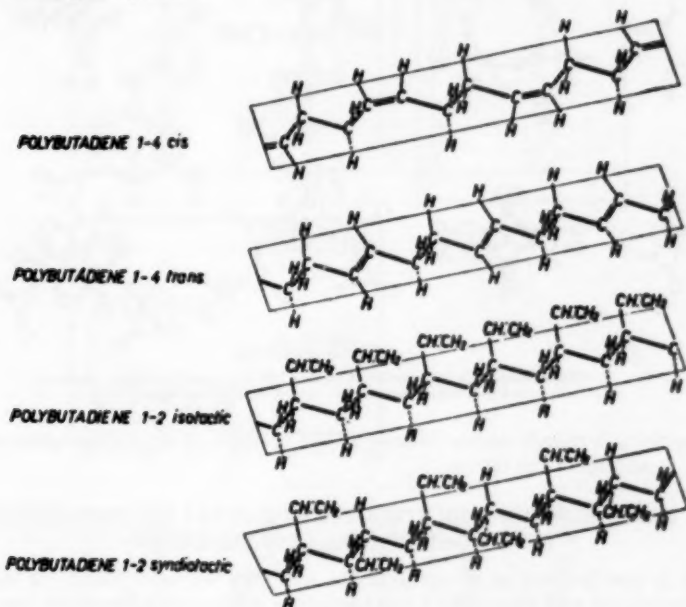


FIG. 5.—Configurations of the four possible regular chains of polybutadiene.

In Figures 5 and 6, we have shown the models of the chains of the four stereoisomeric polymers of butadiene whose main chains are arbitrarily stretched on a plane (Figure 5) and the conformations they actually assume in the crystalline state (Figure 6). All the observed conformations satisfy the principle of the staggered simple bonds, also for the carbon atoms adjacent to the double bond.

The packing of the chains occurs for 1,2 syndiotactic polybutadiene and for *cis*-1,4 polybutadiene, whose chains contain glide planes with translation along the fiber axis, by a regular juxtaposition of the chains on these planes. These planes pack themselves one near another so that each chain has the highest number of neighboring chains structurally equivalent among themselves.

For the *trans*-1,4 polybutadiene, the almost filiform chains are packed together in a pseudo-hexagonal lattice, while for the isotactic 1,2 polybutadiene,

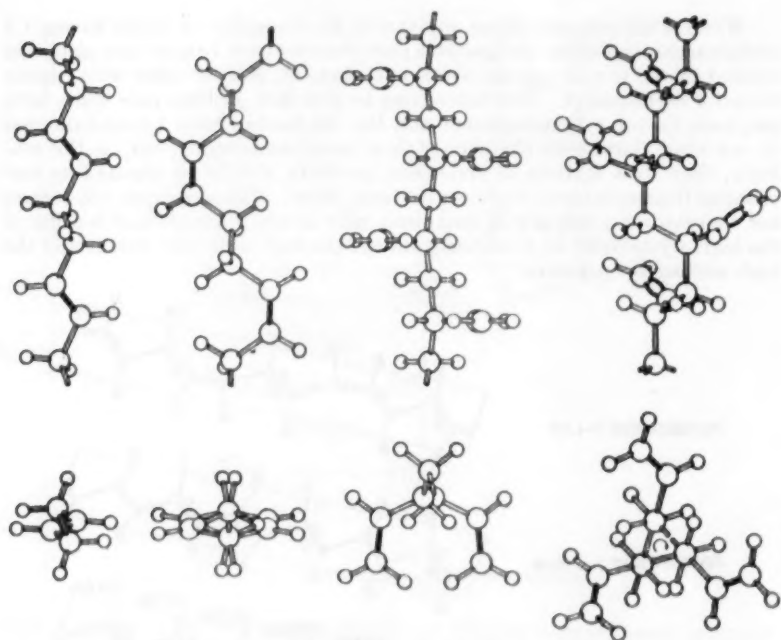


FIG. 6.—Conformations in the crystalline state of the four possible regular chains of four known polybutadienes (*trans*-, *cis*-1,4, syndio-, isotactic 1,2).

the packing is rhombohedral because of the presence of crystallographic screw axes, 3_1 and 3_2 , in the lattice.

3. COMPARISON OF THE STRUCTURE OF *CIS*-1,4 POLYBUTADIENE WITH THAT OF *CIS*-1,4 POLYISOPRENE

It is also interesting to compare the structure we have found for *cis*-1,4 polybutadiene with that of *cis*-1,4 polyisoprene in the crystalline state (natural rubber).

The crystalline structure of natural rubber has been studied several times by many authors; but now it appears definitely resolved owing, above all, to the works performed by Bunn¹⁰ and Nyburg⁹. Natural rubber, according to the latter, has a monoclinic unit cell, with axes at 90° , space group $P2_1/a$.

However, after examining the co-ordinates of the ten atoms of two monomeric units describing the independent structural unit (x, y, z) according to Nyburg, it may be easily noted that they are not independent one of another; the independent unit is actually formed by only one monomeric unit in x, y, z which along the chain is followed by another one in $\frac{1}{2} - x, y, \frac{1}{2} + z$. Under this condition (implicit in the Nyburg co-ordinates) the space groups must be chosen as $Pbca$, which adds to the four general positions of $P2_1/a$ the other four obtainable by effecting the transformation $(\frac{1}{2} - x, y, \frac{1}{2} + z)$ on themselves. Also, according to Nyburg, molecules described by x, y, z co-ordinates, may be statistically replaced by the corresponding molecules having co-ordinates

($x, \frac{1}{2} - y, z$). Only by this assumption it has been possible to obtain a good agreement between experimental and calculated intensities.

Nevertheless, the hypothesis of a completely random vicariance in the same crystal site of mirrored macromolecules in respect to the plane $y = \frac{1}{2}$ does give rise to some unsuitable Van der Waals contacts ($< 3.2 \text{ \AA}$) between carbon atoms of different chains.

The difficulties are less if, instead of an isomorphous statistical substitution of the single chain, we consider an isomorphous statistical substitution of two different types of layers of monomolecular thickness.

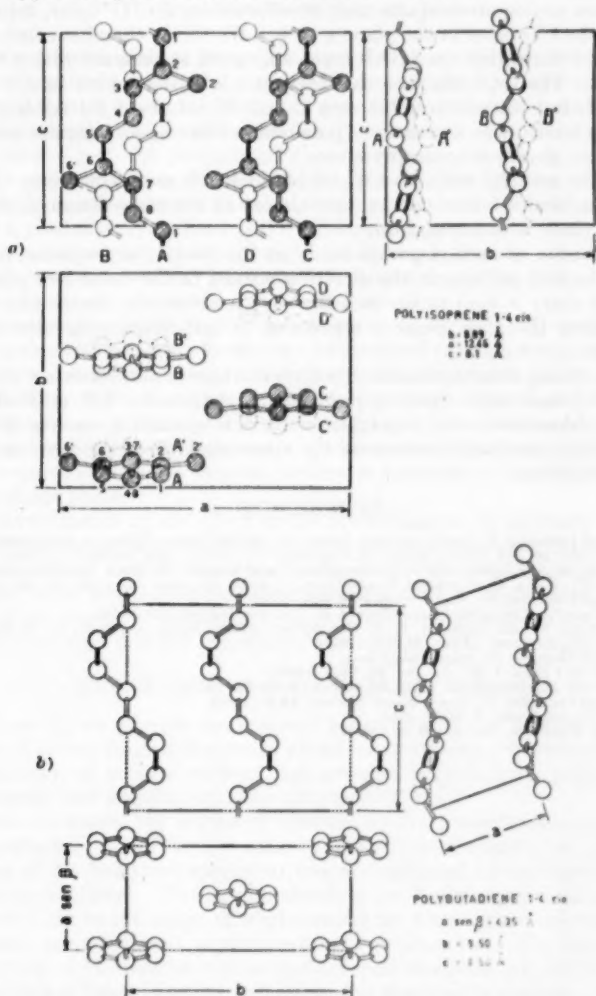


Fig. 7.—Comparison between the crystal structures of *cis*-1,4 polyisoprene and that of *cis*-1,4 polybutadiene.

Let us consider (Figure 7) the succession of molecules ABA, that can be described by the space group *Pbac* on the projection on *ab* and *ac*. All the carbon atoms of the molecules are interested in intermolecular contacts and these contacts do not overcome those we have found for *cis*-1,4 polybutadiene.

A layer of molecules CDC . . . packs, according to the space group *Pbac*, with the layer ABA. The contacts between C and D are analogous to those between A and B.

The contact of the molecule C with the molecules A and B is effected, on the contrary, only by the methyl group.

But then analogous contacts may be effected by a C'D' layer, mirrored in respect to the CD layer in the plane $y = \frac{1}{2}$. We think, therefore, that there is evidence to believe that an ABAB layer may pack at pleasure with a CD or a C'D' layer. The total effect on the intensities is as if a mirror in $y = \frac{1}{2}$ actually existed; but the contacts between C and D' (of about 3.1 Å), implied by the Nyburg model, who assumes the possibility of having an irregular succession CDC'D . . . does not occur any more.

Thus, the analogy with *cis*-1,4 polybutadiene is more complete. In both cases the molecules follow one another almost at the same distance, along the symmetry plane with translation.

The presence of methyl groups leads, in the *cis*-1,4 polyisoprene, to an increase of the unit cell size in the direction normal to the symmetry plane with translation $c(a_{PI} > v_{PB})$ to the fact that b_{PI} is about the double of $a \sin \beta_{PB}$ because along the glide plane a succession of anticlinal molecules must be represented.

We can finally observe that in all polymers whose chains contain a symmetry plane with translation (polyvinylchloride, syndiotactic 1,2 polybutadiene, *cis*-1,4 polybutadiene, *cis*-1,4 polyisoprene), this symmetry element is kept in the crystalline state and determines the space packing of the macromolecules among themselves.

REFERENCES

- ¹ Natta, G. and Corradini, P., *Rend. Acc. Naz. Lincei* **19**, (18) 228 (1955); Natta, G. and Corradini, P., *J. Polymer Sci.* **20**, 251 (1956); Natta, G., Corradini, P., Porri, L. and Morero, D., *Rend. Acc. Naz. Lincei* **20** (8), 560 (1956); Natta, G., Corradini, P. and Bassi, I. W., *Rend. Acc. Naz. Lincei* **23** (8), 363 (1957); Natta, G., Corradini, P. and Porri, L., *Rend. Acc. Naz. Lincei* **20** (8), 728 (1956).
- ² Natta, G. and Corradini, P., *Angew. Chemie* **68**, 615 (1956).
- ³ Natta, G., Porri, L., Corradini, P. and Morero, D., *Chim. e Ind.* **40**, 362 (1958).
- ⁴ Natta, G., Porri, L. and Corradini, P. *It. Pat.* 566940 (1956); Natta, G., Porri, L., Mazzei, A. and Morero, D., *La Chim. e l'Ind.* **41**, 398 (1959).
- ⁵ Natta, G. and Moraglio, G., unpublished data.
- ⁶ Corradini, P. and Bassi, I. W., *Ric. Sci.* **28**, 1435 (1958).
- ⁷ *Int. Tabellen zur Bestimmung von Kristallstrukturen*, 2 (Berlin, 1935).
- ⁸ Natta, G. and Corradini, P., *Suppl. Nuovo Cimento*, **15**, 9 (1960).
- ⁹ Nyburg, S. C., *Acta Cryst.*, **7**, 385 (1954).
- ¹⁰ Bunn, C. W., *Proc. Roy. Soc., A* **180**, 40 (1942).

EFFECT OF CRYSTALLIZATION OF POLYMERS ON DIELECTRIC LOSS *

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One structural feature of crystallizing polymers is the existence within them of a crystalline and an amorphous phase. To explain the peculiar structure of these substances it is valuable to study the effect of crystallization upon the character of the thermal motion of the macromolecules. It was to be expected that the mobility of the portions of the macromolecules which were in the crystalline and amorphous phases would be different. In addition, the thermal motion of the macromolecules in an amorphous polymer and in the amorphous phase of a partially crystallized polymer likewise might differ.

To explain these questions we might study many physical properties such as specific heat and nuclear paramagnetic resonance. But in the literature there are practically no contributions to this subject.

We showed previously¹ that in the majority of crystallizing polymers two forms of dielectric relaxation losses may be observed: 1) high frequency relaxation losses, which will take place in the glassy state of the amorphous phase and which reflect the thermal motion of quite small portions of macromolecules such as separate groups or links, and 2) medium frequency relaxation losses, which are observed at temperatures above the vitrification temperature (T_g) and which may be connected with the thermal motion of segments of macromolecules in the amorphous phase.

The investigation of the effect of the crystallization of polymers upon the dielectric losses makes it possible therefore to get information on the alternation of the character of thermal molecular motions due to crystallization.

On the other hand, such investigations also have a practical value, since changes in the degree of crystallinity may have a considerable effect upon the dielectric properties and the manufacture of certain radio components.

EXPERIMENTAL DATA AND DISCUSSION

In Figure 1a, we give the temperature dependence of the tangent of the loss angle, $\tan \delta$, in the medium frequency range for specimens, with varying degree of crystallinity, of natural rubber, high pressure polyethylene, poly(ethylene terephthalate) and polychlorotrifluoroethylene (F-3).

In order to reduce the degree of crystallinity the polyethylene, poly(ethylene terephthalate) and F-3 were cooled rapidly from the melt, i.e., quenched. Annealing of the tempered specimens was accompanied by an increase in the degree of crystallinity². The measurements of $\tan \delta$ of the quenched specimens were carried out in the range of temperatures for which, over the time of the experiment, no additional crystallization was observed. To increase the crystallization of the natural rubber that polymer was stretched 5-fold, and the measurements of $\tan \delta$ were carried out on the stretched specimen.

* Translated by R. J. Moseley from *Vysokomolekulyarnye Soedineniya*, Vol. 1, pages 29-35, 1959.

From Figure 1a, we see that there is a maximum in the curves of $\tan \delta$ vs. temperature obtained at constant frequency. Judging by the temperature range, the maximum is due to medium frequency relaxation losses. As the degree of crystallinity is raised the maximum for natural rubber, poly(ethylene terephthalate) and F-3 moves toward higher temperatures. Thus the temperature at the maximum for poly(ethylene terephthalate) rises by 20° , and for F-3 by 25° . Analogous data had previously been obtained for polychloroprene⁸. Thus with natural rubber, poly(ethylene terephthalate), polychloroprene, and F-3 the relaxation time connected with medium frequency relaxation losses increases with crystallization.

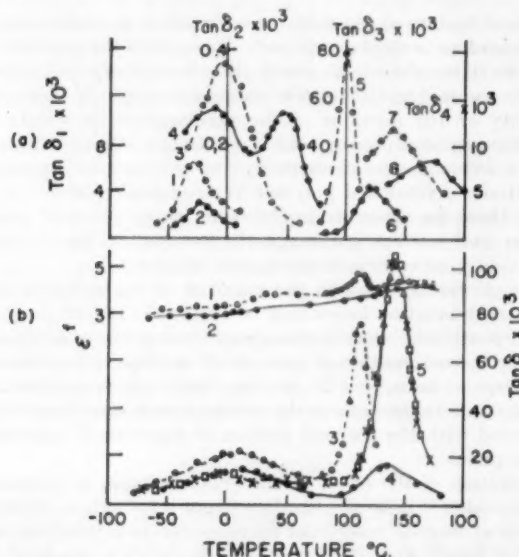


FIG. 1.—Dependence of the loss tangent, $\tan \delta$, and of the dielectric constant, ϵ' , of crystallizing polymers upon temperature. a) 1 and 2— $\tan \delta$, natural rubber, unstretched and stretched 5-fold (frequency $f = 15 \cdot 10^6$ /s); 3 and 4— $\tan \delta$, polyethylene, quenched and annealed specimens (10^6 /s); 5 and 6— $\tan \delta$, poly(ethylene terephthalate), quenched and annealed specimens ($3 \cdot 10^6$ /s); 7 and 8— $\tan \delta$, polychlorotrifluoroethylene, quenched and annealed specimens ($4 \cdot 10^6$ /s). b) 1 and 2— ϵ' , poly(ethylene terephthalate), quenched and annealed specimens ($6 \cdot 10^6$ /s); 3 and 4— $\tan \delta$, poly(ethylene terephthalate), quenched and annealed specimens ($7 \cdot 10^6$ /s); 5— $\tan \delta$, poly(vinyl ethylal), quenched and annealed specimens ($7 \cdot 10^6$ /s).

Alteration in the degree of crystallinity of polyethylene has a somewhat different effect. From Figure 1a, we see that with $t > t_g$ for a quenched specimen of polyethylene we again have a maximum of medium frequency relaxation losses. After annealing, the losses in the range of the maximum increase, while at a higher temperature a second maximum of $\tan \delta$ becomes apparent. A characteristic of high pressure polyethylene is that the relaxation time for some portions of the macromolecules does not alter on annealing of the quenched specimens (the maximum is close to 0° on Curve 4 in Figure 1a). To explain the nature of this phenomenon we need more detailed investigations of the structure and dielectric properties of polyethylene.

As has been pointed out, the medium frequency relaxation losses are connected with the segmental thermal motion of the portions of macromolecules which are in the amorphous phase. Consequently, crystallization leads to an

increase in the relaxation time of the medium frequency relaxation losses or to a reduction in the mobility of the segments in the amorphous phase.

In Figure 2 we show the dependence of the logarithm of the frequency, $\log f_m$, of the maximum of $\tan \delta$ upon $1/T$, where T is the absolute temperature for the quenched and annealed specimens of poly(ethylene terephthalate) and F-3. The slopes of the lines $\log f_m = \phi(1/T)$ with the quenched and annealed specimens are identical within the given range of temperatures.

From this it follows that the increase in the relaxation time with crystallization is due to the increase in the pre-exponential factor in the well-known equation

$$\tau = A_1 e^{u/RT} \quad (1)$$

It is usually considered that A_1 in Equation 1 depends upon the entropy of activation, i.e., the increase in the relaxation time of the medium frequency relaxation losses on crystallization is connected with a change in the entropy of activation. To explain such changes it is necessary to carry out further investigations into the effect of crystallization upon dielectric losses.

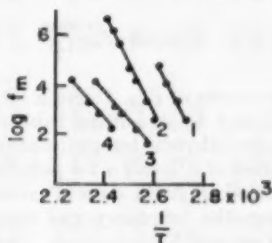


FIG. 2.—Dependence of logarithm of frequency f_m of the $\tan \delta$ maximum upon the inverse absolute temperature $1/T$. 1 and 2—poly(ethylene terephthalate); 3 and 4—polychlorotrifluoroethylene; 1 and 3, quenched; 2 and 4, annealed specimens.

In Figure 1b we give the temperature dependence of $\tan \delta$ for quenched and annealed specimens of poly(ethylene terephthalate) in a wide temperature range (Curves 3 and 4). The maxima in these curves close to 0° correspond to the high frequency relaxation losses, and those with $t > 80^\circ$ to medium frequency relaxation losses. From Figure 1b it follows that on crystallization the temperature of the maximum of $\tan \delta$ for high frequency relaxation does not alter, while for medium frequency relaxation it increases.

It has already been demonstrated in the case of F-3 that annealing of quenched specimens does not alter or even decreases the relaxation time for high frequency relaxation losses.

Thus the crystallization of polymers varies in its effect upon the mobility of segments in the amorphous phase and in quite small portions of macromolecules, whose thermal motion is due to high frequency relaxation losses. If the mobility for segmental thermal motion on crystallization decreases, for the second form of thermal motion this mobility either does not change or even increases.

From Figure 1 we see that the values of $\tan \delta$ and of the dielectric constant, ϵ' , decrease on crystallization in the range of medium frequency relaxation and high frequency relaxation losses. For an analysis of these data as a first approximation we may make use of the theory of dielectric losses and of polarization⁶. According to this theory the magnitude of an imaginary part $\epsilon'' = \epsilon'$. $\tan \delta$ of a complex dielectric constant is connected with the molecular parameter

in the following way:

$$\epsilon''_m = \left[\frac{1.53 \cdot 10^{16} \cdot \frac{n_D + 2}{2 + \frac{n_D^2}{\epsilon'^2_m + \epsilon''^2_m}}}{\mu_{eff}^2 \cdot \frac{n_0 \alpha}{T}} \right] \quad (2)$$

Here n_0 and μ_{eff} are respectively the concentration and effective dipole moment of a link of the polymeric molecule, T is the absolute temperature, n_D the refractive index, ϵ'_m and ϵ''_m the real and imaginary parts of the complex dielectric constant in the range of the maximum losses, α the distribution parameter of the relaxation times. This parameter indicates the breadth of the relaxation spectrum for the given form of loss.

The term in the square brackets in Equation 2 alters by 3 to 5% at the most on crystallization. The magnitude of the effective dipole moment depends mainly upon the structure of the macromolecule. It is however not ruled out that the value of μ_{eff} may alter somewhat on crystallization. Therefore Equation (2) may be represented as follows:

$$\epsilon'' = \text{const} \cdot \mu_{eff}^2 \cdot \frac{n_0 \alpha}{T} \quad (3)$$

In Table I we give the values of ϵ''_m , T and α for specimens with different degrees of crystallinity, X_0 and X_1 , of natural rubber, vulcanized natural rubber, polychloroprene and poly (ethylene terephthalate) in the medium frequency relaxation range. The values of ϵ''_m and α for polychloroprene and vulcanized natural rubber were calculated from the data in earlier papers^{3,4}. The parameter α was determined from the frequency and temperature dependences, ϵ' and ϵ'' , according to other papers^{5,6}.

In Table I we also give the values

$$A = \frac{\epsilon''_{m1}}{\epsilon''_{m0}}; \quad B = \frac{\alpha_1}{T_1} \div \frac{\alpha_0}{T_0} \quad \text{and} \quad C = B \frac{1 - X_1}{1 - X_0}$$

The subscript 1 relates to specimens with a high degree of crystallinity, while subscript 0 relates to specimens with a lower degree.

The value A characterizes the reduction in dielectric losses on raising the degree of crystallinity from X_0 to X_1 . The constant B shows how the losses alter as a result of the dependence of ϵ'' upon α and T . If, for instance, $B = 0.5$, this means that as a result of the alteration of α and T , ϵ''_m is reduced to half.

From Table I we see that with an increase in the degree of crystallinity the magnitude of the distribution parameter α of the relaxation times for the medium frequency relaxation losses decreases, but hardly changes for high frequency relaxation losses. In addition, in every case $A < B$, i.e. the reduction in the high frequency relaxation and medium frequency relaxation losses on crystallization cannot be attributed only to an alteration in α and in the temperature of the maximum (of relaxation time). However in the case of medium frequency relaxation the reduction in α and increase in T on crystallization brings about a certain reduction in the magnitude of ϵ''_m . For instance, with poly(ethylene terephthalate) ϵ''_m is reduced on crystallization to one quarter ($A = 0.25$); alterations in α and T caused a reduction of ϵ''_m to one half ($B = 0.5$). Analogous data are obtained for the other polymers as well (see Table I).

TABLE I
RESULTS OF DIELECTRIC LOSS MEASUREMENTS

Type of loss	Polymer	$f_m, \text{c/s}$	Type I with least degree of crystallinity				Type II with greatest degree of crystallinity				Notes
			X_0	$\epsilon''_{\infty 0}$	T_0	α_0	X_1	$\epsilon''_{\infty 1}$	T_1	α_1	
Med. freq. relaxation	Natural rubber	$2.3 \cdot 10^4$	~ 0	0.016	261	0.38	0.28	0.0075	263	0.31	Type II stretched 5-fold
		$1.5 \cdot 10^4$	~ 0	0.016	245	0.39	0.28	0.0073	248	0.30	
	Vulcanized natural rubber	$16 \cdot 10^4$	~ 0	0.045	262	0.31	0.04	0.030	262	0.30	Type II stretched 2.5-fold
		$5 \cdot 10^4$	~ 0	0.045	257	0.32	0.04	0.031	258	0.29	
Med. freq. relaxation	Polychloroprene	$2 \cdot 10^4$	~ 0	0.046	253	0.38	0.04	0.031	254	0.32	Type II stretched 2.5-fold
		10^4	~ 0	1.0	258	0.48	0.04	0.75	259	0.43	
	Polyethylene terephthalate	10^4	—	—	—	—	0.19	0.66	258	0.36	Type II stretched 2.2-fold stretched 4.5-fold stretched 7-fold
		10^4	—	—	—	—	0.36	0.58	259	0.32	
High freq. relaxation	F-3	$5 \cdot 10^4$	~ 0	0.49	368	0.48	0.60	0.12	386	0.24	Type II quenched
		$3 \cdot 10^4$	~ 0	0.48	373	0.54	0.60	0.12	390	0.28	
	Polyethylene terephthalate	$2 \cdot 10^4$	~ 0	0.45	379	0.44	0.60	0.11	398	0.22	Type II annealed
		$2 \cdot 10^4$	~ 0	0.070	281	0.20	0.45	0.054	263	0.20	
High freq. relaxation	F-3	$2 \cdot 10^4$	~ 0	0.12	333	0.50	0.45	0.078	323	0.50	do.
		$4.5 \cdot 10^4$	~ 0	0.13	369	0.60	0.45	0.082	367	0.60	
	Polyethylene terephthalate	$6.0 \cdot 10^4$	~ 0	0.067	273	0.30	0.60	0.041	273	0.31	do.
		$6.5 \cdot 10^4$	~ 0	0.055	279	0.31	0.60	0.039	280	0.28	

This discrepancy between the changes in α and T on the one hand and in ϵ''_m on the other which takes place on crystallization is caused by the transition of the relaxing portions of the macromolecules into the crystalline phase. In point of fact the crystalline phase is characterized by denser packing than is the amorphous. As a result of this the mobility of the portions of macromolecules on transition into crystallites decreases, while the relaxation time probably becomes so much greater that these portions of the macromolecules do not take part in the relaxation processes of the medium frequency relaxation and high frequency relaxation losses. Since the loss data are connected with the amorphous phase, the concentration of polar groups corresponding to them is directly proportional to the amount of substance in this phase.

$$n_0 = C(1 - X) \quad (4)$$

The value C in Table I characterizes the change in ϵ''_m as a result of dependence upon α , T and n_0 . In its turn the latter is connected with the degree of crystallinity by Equation (4).

If ϵ''_m changes on crystallization only as a function of α , T and n_0 , then the equivalence $A = C$ must apply.

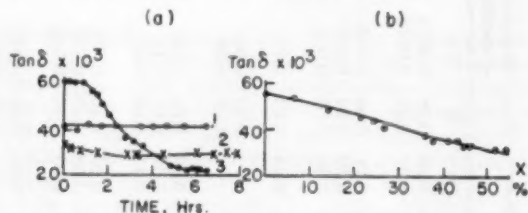


FIG. 3.—Dependence of $\tan \delta$ of poly(ethylene terephthalate) upon time, and of $\tan \delta$ of polychlorotrifluoroethylene upon the degree of crystallinity X . a) $\tan \delta$ vs. time; poly(ethylene terephthalate); 1—91°, 2—104°, 3—118°, frequency $6 \cdot 10^4$ c/s. b) $\tan \delta$ vs. X , F-3, frequency $8 \cdot 10^4$ c/s, temperature 79°.

It must be noted that this equivalence has an approximate character, if only because the values for the degree of crystallinity X_0 and X_1 were taken from other papers⁷. In addition, in crystallization there may be a change in the value of the effective dipole moment on crystallization. Nevertheless, as may be seen from Table I, the actual change in ϵ''_m on crystallization is in a number of cases quite close to the value calculated ($A \cong C$).

Thus the reduction in the values of the high frequency relaxation and medium frequency relaxation losses on crystallization is brought about by a reduction in the number of polar portions of macromolecules which are in the amorphous phase. At the same time, in the case of medium frequency relaxation it is partially connected with an increase in the breadth of the relaxation spectrum (a reduction in α).

The above data on the effect of crystallization upon dielectric losses were obtained by comparison of quenched and annealed specimens of polyethylene, poly(ethylene terephthalate), and F-3. The changes in ϵ' and $\tan \delta$ on thermal treatment of this polymer are fully reversible and may be observed repeatedly in one and the same specimen.

Since these changes may not be connected exclusively with crystallization phenomena, we measured the dielectric losses of quenched and annealed specimens of a typical amorphous polymer—poly(vinyl ethylal) over a wide range of temperatures. From Curve 5 of Figure 1b, which was plotted from

these data, we see that annealing and quenching an amorphous polymer has no effect upon the value of $\tan \delta$ in the range of relaxation losses of both types, i.e., the observed changes in the value of $\tan \delta$ on thermal treatment of crystallizing polymers are connected with crystallization phenomena.

The reduction in the value of the dielectric losses and of ϵ' due to crystallization may be used to study certain factors in the crystallization of polymers. For instance, by observing the dependence of ϵ' or $\tan \delta$ upon time in the melting or crystallization ranges, at constant temperatures, it is possible to draw conclusions as to the kinetics of these processes.

In Figure 3a, we give the time dependence of $\tan \delta$ of quenched poly(ethylene terephthalate) at three different temperatures above t_g . It may be seen that at 91° and 118° the values of $\tan \delta$ does not alter with time almost for 8 hr. At 104°, $\tan \delta$ remains constant for approximately one hour, and then for a space of 4 hr we observe a reduction in $\tan \delta$ to a certain constant value. Since the medium frequency relaxation and high frequency relaxation dielectric losses decrease on crystallization of polymers, it follows from these data that for the crystallization of quenched poly(ethylene terephthalate) at 91° we require standing for more than 8 hr., at 104° something of the order of 5 hr. and at 118° less than 10 to 15 min. Within these periods of time the specimens are kept at the respective temperatures up to the beginning of measurement.

The data presented agree with the results of investigations of the kinetics of crystallization of poly(ethylene terephthalate) by other methods^{2,3}.

For polar polymers the value of $\tan \delta$ in the range of the maximum of medium frequency relaxation and high frequency relaxation losses is unequivocally connected with the degree of crystallinity³, Figure 3b. Therefore the dielectric method may be employed for the determination of the degree of crystallinity of polar polymers.

CONCLUSIONS

The values of ϵ' and $\tan \delta$ in the range of dielectric losses of relaxation character decrease on crystallization of polymers. In the case of medium frequency relaxation losses $\tan \delta$ sometimes decreases 2 to 4 fold and ϵ' by 20 to 30%. This is mainly connected with transition of polar portions of macromolecules into crystallites, on the one hand, and on the other hand with an increase in the breadth of the relaxation spectrum for the polar groups remaining in the amorphous phase.

The relaxation time for the medium frequency relaxation dielectric losses, connected with the thermal motion of segments of macromolecules, in the amorphous phase, increases on crystallization, while for high frequency relaxation losses, reflecting the thermal motion of separate groups or links, does not change or indeed even decreases.

The dielectric method may be used for the investigation of the kinetics of crystallization and melting of polymers and, in the case of polar polymers, also for the determination of the degree of crystallinity.

REFERENCES

- ¹ Mikhailov, G. P. and Sashin, B. I., *Vysokomolekulyarnye Soedineniya* 1, 9 (1959).
- ² Kaufmann, H. S., Cobbs, W. H., Jr. and Burton, R. L., *J. Am. Chem. Soc.* 75, 1477 (1953); *J. Polymer Sci.* 10, 275 (1953).
- ³ Mikhailov, G. P. and Fainshtein, B. M., *Zhur. Tekh. Fiz.* 22, 759 (1952); 21, 1395 (1951).
- ⁴ Mikhailov, G. P. and Sashin, B. I., *Zhur. Tekh. Fiz.* 26, 1723 (1956).
- ⁵ Fuoss, R. and others, *J. Am. Chem. Soc.* 63, 385 (1941); Mikhailov, G. P., and Sashin, B. I., *Zhur. Tekh. Fiz.* 25, 1696 (1955).
- ⁶ Fattakhov, K. Z., *Zhur. Tekh. Fiz.* 22, 313 (1952).
- ⁷ Coppel, J. M. and others, *RUBBER CHEM. & TECHNOLOGY*, 23, 310 (1950); Reddish, W., *Trans. Faraday Soc.* 46, 459 (1950).
- ⁸ Kolb, H. and Isard, E., *J. Appl. Phys.* 20, 563 (1949).
- ⁹ Mikhailov, G. P. and others, *Kolloid Zhur.* 20, 461 (1958).

THE DIFFUSION THEORY OF ADHESION *

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INTRODUCTION

Processes of bonding and adhering are essential in rubber, paper and plywood manufacture as well as in the artificial leather, aviation and other industries. The use of various adhesives in daily life is well known. In considering the various materials used as adhesives it is interesting to note that all of them are polymers. Thermoplastic and thermosetting resins, natural resins, cellulose derivatives, albumin and rubber are known to be used in adhesive formulations. It is important too that most high molecular weight substances having good adhesive properties have linear molecules. Nonpolymeric adhesives are such inorganic materials as cements and solders but bond formation with these takes place according to a special mechanism (coalescence of crystals, welding) which has little in common with the formation of an organic adherent bond and can only conditionally be considered a type of adhesion. Concerning bonding with liquid glass, it must be remembered that sodium silicate is present in the form of flexible chains in solution, and is therefore a type of inorganic macromolecular substance¹.

The present paper is devoted to a discussion of the mechanism of adhesion of polymers to each other. The practical importance of the problem is enormous. The adhesion of polymers to metals will not be considered since it is probably in most cases a special chemical process and besides, the author has never been directly concerned with the physical chemistry of metal to polymer adhesion.

THEORY

Earlier investigators working in this field have attempted to generalize their results^{1,2}. In most cases these investigations are of little value for the development of theoretical concepts; bonding of surfaces (wood, metal, glass, etc.) usually has been studied by means of liquids and solids whose nature is quite different from the polymers in the now common adhesives. In testing bond strengths little attention has been paid to the type of separation. However, correct observation and evaluation of the type of separation is one of the fundamentals for correct evaluation of adhesion. Finally, older authors attempted to relate adhesion to wetting and approached adhesion incorrectly as a thermodynamically reversible phenomenon.

Remarkable progress has been made during the last few years in the physical chemistry of the adsorption phenomenon with the appearance of (1) *electric* and (2) *diffusion* theories of polymer adhesion. The adsorption theory considers adhesion a purely surface process and explains the formation of strong bonds between adhesive and substrate through intermolecular forces.

Baneroft² commented in 1926 on the role that adsorption plays in the overall problem of adhesion. A complete adsorption theory was developed by De

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Vysokomolekulyarnye Soedineniya*, Vol. 1, pages 230-39, 1959.

Bruyne⁷ and McLaren and coworkers⁸⁻¹². According to McLaren, adhesion can be divided into two stages: The first stage consists in the migration of large polymer molecules from the solution to the surface of the substrate; this process is aided by micro-Brownian motion. As a result the polar groups of the adhesive approach the polar groups of the substrate. Through pressure and lowering of viscosity on heating, the chain segments can approach the surface very closely, even in the absence of solvent. The second stage consists of the sorption process. When the distance between molecules of adhesive and substrate becomes less than 5 Å, intermolecular forces begin to act. This includes the whole "force spectrum", starting with dispersion forces (about 10^2 cal/mole) up to hydrogen bonding with energies in the range of 10^4 cal/mole. The following bonds may be formed: dipole-dipole bonds, as for example in polyvinylchloride, dipole-induced dipole, such as in adhering polystyrene, and hydrogen bonding as in the case of adhesion of polyvinyl alcohol to cellulose.

In spite of the broad recognition that the adsorption theory of adhesion has received¹³, it has several weaknesses: 1. As was shown by Deryagin and coworkers^{14,15}, the work of peeling (force of adhesion) of the adhesive film can reach values as high as 10^4 – 10^6 erg/cm², but the work necessary to overcome molecular forces is only 10^2 – 10^3 erg/cm². In other words, the real work of adhesion is several magnitudes higher than that expected from molecular forces. The attempt to explain this inconsistency by the expenditure of work of deformation of the film on peeling failed. 2. It was shown by Deryagin and Krotova¹⁴ that the work of adhesion depends on the rate of peeling of the adhesive film while the work to overcome the molecular forces must be independent of the rate of separation of the molecules. 3. Adsorption theory does not offer an explanation for the high adhesion between nonpolar molecules. It is well established that such low polarity polymers as polyisobutylene, NR or gutta-percha show good adhesion to a number of substrates. To explain these facts, for which the adsorption theory offers no explanation, Deryagin and Krotova¹⁴ suggested the electric theory of adhesion. According to this theory, the system adhesive-substrate is compared with a condenser, the conducting elements of which are the electric double layers that arise when contacting two different substances. When separation of the adhesive occurs it may be pictured as the separation of the electrodes of the condenser; a difference in potential then develops up to a certain limiting value, where discharge begins. On rapid peeling, the charges do not have time to dissipate, and the high initial charge density is preserved until gas discharge occurs. This then is the basis for the large work of adhesion values according to Deryagin and Krotova, since the action of the attractive forces of positive and negative charges is overcome at relatively large distances. When slow separation takes place as a result of partial removal of charges from the surfaces, the work of adhesion is decreased; Deryagin and Krotova explain the dependence of the work on adhesion on the rate of peeling by such a mechanism. The following are indications that electric phenomena may take place during peeling of polymer seams: electrification of surfaces formed, presence in some cases of electrical charges and electronic emission, decrease of the work of adhesion on irradiation of bonds by X-rays and gamma rays, etc. That adhesion is a purely electrical phenomenon is a viewpoint shared by some investigators abroad¹⁶. However, the electric theory alone cannot explain the adhesion of polymers to each other.

For one thing, surface electrification, gas discharge, electron emission, etc., are not detectable in many cases of separation of adhered polymer pairs. In other cases these phenomena are only observed under special conditions.

Nevertheless, a given pair of polymers are able to form a strong bond even when no electrical phenomena can be observed on separation. Secondly, in the case where the polymers are "dielectrics", it is difficult to see how considerable quantities of electrons can be transferred from one polymer to the other and thereby create a large enough contact potential difference between adhesive and substrate. And, thirdly, it is known that as adhesion between polymers is increased, the more alike their structure is. If the whole phenomenon could be reduced to the formation of an electric double layer, the opposite relationship should be observed: the more alike the polymers are, the lower would be the contact potential difference. Fourthly, if adhesion would solely arise from the electric double layer, adhesion between carbon black loaded polymers would be impossible, since such mixtures are good conductors; however, it is known that such mixtures show good adhesion to each other and also to metals. And finally, as the fifth point in case, it is well known that vulcanization eliminates all ability of polymers to adhere to other materials. This is difficult to reconcile with the electrical theory, since the presence of a small quantity of sulfur should not greatly influence the contact potential. It is our opinion therefore that the electrical theory of adhesion is only applicable in cases where polymers are incompatible, or insoluble in each other. If the polymers are compatible, the case of the polar and nonpolar polymers should be distinguished. When a bond forms between nonpolar polymers, the electrical mechanism is not acceptable since such polymers could not be electron donors. In our opinion, adhesion in this case is caused by the interlacing of the surface macromolecules by mutual diffusion. The double electric layers can arise upon formation of bonds between polar polymers; if the polymer molecules or any of their portions are capable of intense thermal motion, adhesion of the two layers will be a consequence of diffusion. As the time of contact increases, the importance of the first (electrical) mechanism will of course decrease but that of the second will increase as a result of liquification of the contact surfaces and increasing penetration depth of the adhesive's macromolecules into the substrate. Morosova and Krotova came to a similar conclusion. They experimentally investigated the relative importance of electrical and diffusion phenomena in the adhesion of polymers.

According to the diffusion theory originally suggested by the author of this paper¹⁷ and later experimentally proved in collaboration with Pisarenko and Shapovalova¹⁸⁻²⁰, the adhesion of polymers and auto-adhesion can be reduced to the diffusion of chainlike molecules or of their parts and as a result lead to the formation of a strong bond between adhesive and substrate. Auto-adhesion has been discussed in great detail here and abroad^{17, 21-26}. The difference between adhesion and auto-adhesion is the fact that in the former diffusion of two different types of macromolecules occurs while in the latter diffusion of identical molecules takes place. A peculiar and distinguishing feature of the diffusion theory lies in the fact that it involves the most characteristic properties of high molecular weight substances: their chainlike structure, the flexibility of their molecules and their micro-Brownian motion. It is worthwhile to note that as a rule, adhesive molecules have the ability to diffuse. If the adhesive is applied in solution, and the substrate can swell or dissolve in this solution, a remarkable diffusion of the substrate into the adhesive may occur. Both of these processes lead to the disappearance of the distinct interphase separating the two phases and to the formation of a bond presenting a gradual transition from one polymer to the other. Adhesion according to the diffusion theory essentially presents a volume phenomenon. Since the diffusion theory provides

for the formation of a durable transition layer between the adhesive and the substrate it lacks the shortcoming of the adsorption theory; it can easily explain the lack of agreement between the work of peeling and the work required to overcome the molecular surface forces between adhesive and substrate. The diffusion theory allows the interpretation of the dependence of work of adhesion on the rate of peeling for it is well known that the apparent strength of a polymer depends on the rate of degradation (rupture).

It is quite obvious that the diffusion of polymer molecules is nothing but a solution phenomenon. This author¹⁷ was the first to point out the importance of mutual solubility on the adhesion of polymers. He suggested the adhesion of polymers to each other as a criterion for their compatibility. Later Deryagin²⁷ emphasized the relationship between compatibility and adhesion and suggested judging adhesion by compatibility data. Mutual solubility of the components is important for their adhesion and is basically determined by the polarity²⁸; it is in accord with the well known empirical rule of Debroin, according to which strong adhesion is possible only when both polymers are either polar or non-polar and is difficult in the case of one polar and one nonpolar polymer. In general mutual solubility of polymers is determined by heat of mixing.

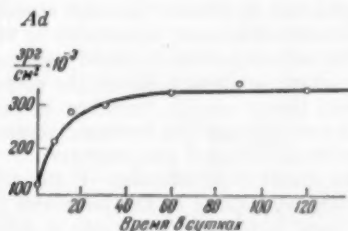


FIG. 1.—Adhesion of copolymer SKN-40 to cellophane vs. time, plotted from the moment of preparation of the bond to its testing. Ordinate: Adhesion, $\text{erg}/\text{cm}^2 \times 10^{-3}$. Abscissa: Time, days (24 hours).

EXPERIMENTAL

In addition to general considerations that confirm the correctness of the diffusion theory of adhesion, there are a series of experimental facts and observations that confirm it. Let us consider some of them.

The effect of contact time.—Little attention has so far been paid to the contact time between adhesion and substrate. However, the effect of this contact time bears the best proof for the diffusion theory of adhesion. Figure 1 shows typical curves of the variation of butadiene-acrylonitrile copolymer SKN-40 adhesion to cellophane as a function of time from the moment of bonding to the moment of separation (peeling). The force of adhesion between the polymeric adhesive and the macromolecular substrate increases with time, rapidly at first and progressively slower, approaching finally a certain limiting value. This characteristic increase of adhesive force as function of time cannot be explained by either adsorption nor the electrical theory. The diffusion theory can explain this behavior readily by the slow penetration of "cumbersome" macromolecules of adhesive into the substrate.

Effect of bonding temperature of thermal treatment on adhesion.—In Figure 2 a typical curve is given that shows the characteristic dependence of adhesion on the temperature to which the bonded samples of cellophane with SKN-40 were

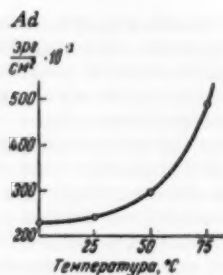


Fig. 2.—Adhesion of copolymer SKN-40 to cellophane vs. temperature to which the samples were heated. Ordinate: Adhesion, $erg/cm^2 \times 10^{-3}$. Abscissa: Temperature, $^\circ C$.

heated. The samples were prepared by spreading a solution of the adhesive on cellophane, drying the assembly at or near 0° ; before peeling, they were heated at different temperatures for 40 minutes. Throughout the temperature investigated, adhesion increased on heating without approaching a limiting value. Increased adhesion on heating cannot be explained by an increase in true contact surface, since on spreading an adhesive solution already forms a maximum surface area. Neither is such an increase explainable by the adsorption theory, since the spreading of the adhesive solution would assure complete orientation of its molecules on the substrate already during the preparation of the bond. In contrast, the diffusion theory readily furnishes an explanation of the increased adhesion in this case through the increased thermal motion of macromolecules or their segments at elevated temperatures.

Effect of the molecular weight of the adhesive.—If the diffusion theory is correct, the molecular weight and shape of the molecules involved must effect adhesion since both of these factors affect the rate of diffusion. It also holds true that according to the adsorption or electrical theory, these factors should not have any large effect on the force of adhesion. Experiments have shown that in accordance with the diffusion theory, adhesion actually is dependent on the molecular weight. Table I gives data illustrating variation of adhesion of different molecular weight polyisobutylene to cellophane.

It becomes apparent that adhesion of polyisobutylene of molecular weight 7000 is practically zero; this type of peeling may therefore be termed purely cohesive; it is possible because of the low cohesive strength of the above polyisobutylene. On increasing the molecular weight of the polyisobutylene, peel resistance sharply increases, reaching 369 g/cm at 20,000. Peeling type may be termed mixed; obviously, the cohesive strength in this case is approximately equal to the peel resistance of the adhesive from the substrate. On increasing

TABLE I
ADHESION OF A SERIES OF DIFFERENT MOLECULAR WEIGHT
POLYISOBUTYLENES TO CELLOPHANE

Molecular weight of polyisobutylene	Type of peeling	Adhesion g/cm
7000	Cohesive	0
20,000	Mixed	369
100,000	Adhesive	67
150,000	Adhesive	67
200,000	Adhesive	68

the molecular weight of polyisobutylene to 100,000 the force of adhesion drops to 67 g/cm and becomes purely adhesive in character. Further increase in molecular weight changes neither type nor strength of adhesion. The fact that adhesive strength was independent of the adhesive's molecular weight after the latter had reached a certain value had been observed by other investigators with quite different substances⁸⁻¹⁰. From the point of view of the diffusion theory this phenomenon must be explained in a similar fashion as the case of auto-adhesion²⁴: on increasing the molecular weight, the number of free molecular ends that are able to diffuse with special ease is decreasing. At sufficiently high molecular weight, mostly the molecular centers will diffuse into the substrate; they have difficulty penetrating between the molecules of the substrate. That is the reason why for the same contact time less durable bonds between the polymers are formed. Since the size of the diffusion center

TABLE II
ADHESION OF DIFFERENT ADHESIVES TO CELLOPHANE

Name of adhesive and structure	Type of peeling	Adhesion g/cm
Polybutadiene		
50% 1,4		
50% 1,2	Adhesive	1495
Polybutadiene (same molecular weight as above)		
20% 1,4		
80% 1,2	Mixed	550
Copolymer		
70% Butadiene		
30% Styrene	Cohesive	1368
Copolymer		
50% Butadiene		
50% Styrene	Adhesive	14
Copolymer		
70% Butadiene		
30% Methylstyrene	Mixed	771

portions of the macromolecules is independent of the length of the molecules, adhesion becomes independent of molecular weight. From the above data it could be concluded that adhesion is higher the lower the molecular weight of the polymer. This deduction can be easily understood on the basis of the diffusion theory: when the size of the molecules is decreased, their ability to diffuse increases, and therefore adhesion must increase. However, since with decreasing molecular weight their cohesive strength decreases, polymers of medium molecular weight must have optimum bonding ability; they are able to form strong bonds and have at the same time a sufficiently high cohesive strength to make a good adhesive.

Effect of molecular shape.—In Table II results are given that were obtained from cellophane strips bonded together with different nonpolar and weakly polar adhesives of different molecular structure. These data show polybutadienes with increasing 1,2 polymer content give poorer adhesives. This phenomenon is explained by the larger amount of 1,2-polybutadiene giving the molecules poorer diffusion ability due to purely steric factors based on the increase in

vinyl side chains. Another example of the influence of side chains on adhesion is illustrated in the same table; copolymers of styrene and butadiene with various monomer ratios were examined for their ability to adhere to cellophane. A small amount of styrene in the copolymer leads to increased adhesion, while larger quantities show a decrease. Similar variations in adhesion by varying the comonomer ratio were observed by other investigators²⁹. This may be explained by the fact that copolymer molecules with a small amount of styrene have a regular structure that facilitates diffusion of the adhesive into the substrate. A large amount of styrene groups in the copolymer molecule lowers its ability to diffuse due to the presence of a large number of bulky side chains (phenyl groups) and a decreased chain flexibility. Substitution of styrene by methylstyrene also leads to a decrease in adhesion. The reason for this is the decrease in diffusion rate of the macromolecules because of the presence of additional methyl groups. The presence of short side groups in macromolecules generally lowers its adhesion. However, if side chains are sufficiently long, they can play the part of separate chains and they will then for steric reasons diffuse with greater ease into the substrate than the center parts of the macro-

TABLE III
ADHESION OF BUTADIENE-ACRYLONITRILE COPOLYMERS OF
VARYING POLARITY TO CELLOPHANE

Per Cent acrylonitrile units in copolymer	Type of peeling	Adhesion, g/cm
18.4	Cohesive	1638
28.6	Mixed	1382
37.7	Adhesive	132

molecules. The correctness of this assumption is confirmed by the data of McLaren^{8, 10}, who established that adhesion to cellophane is increasing in a series of polymethacrylates from polymethylmethacrylate to poly-*n*-butylmethacrylate. McLaren also showed that poly-isopropylmethacrylate and poly-isobutylmethacrylate have considerably poorer adhesion to cellophane than the corresponding poly-*n*-alkylmethacrylates. This is in good agreement with our concept of macromolecular shape and its effect on adhesion. Two conclusions may be drawn on the effect of molecular shape on adhesion. 1. The absence of branching and regular molecular structure in general tends to increase adhesion, since flexibility and mobility of the molecular chains is increased. If the polymer consists of molecules of very regular structure and is capable of crystallization, its adhesion becomes insignificant. As an example one can take amorphous polyisobutylene and crystalline polyethylene. While the former has remarkably high adhesion, polyethylene at room temperature shows none. 2. Three dimensional (crosslinked) polymers are incapable of adhesion. This is clearly because the crosslinks connecting the main chains make their diffusion into the substrate impossible. This conclusion is confirmed by the complete absence of adhesive ability found in rubber after vulcanization.

The effect of polarity in macromolecules.—On considering the effect of polarity of an adhesive material on its adhering ability one must first note that experiments show that such nonpolar or weakly polar polymers as polyisobutylene and polybutadiene show remarkably strong adhesion to the polar cellophane. In our opinion this may be explainable by the presence of spaces between the molecules of amorphous cellophane. The flexible molecules of the adhesive

can diffuse into these spaces. Another interpretation of this phenomenon may be a certain degree of solubility of the hydrocarbon chains in cellulose and thereby formation of a bond between substrate and adhesive.

We have furthermore established that with a polar substrate, increasing the polarity of the adhesive actually decreases adhesion. This can be seen from data in Table 3 which show that the butadiene-acrylonitrile copolymer shows less adhesion to cellophane the higher is its acrylonitrile content. At first glance this observation seems hard to understand. It might be assumed that the larger acrylonitrile content would make the copolymer better soluble in polar cellophane and thereby increase adhesion. This contradiction may be readily explained; an increase of polarity of the adhesive increases the rigidity of its molecules and thereby decreases their ability to diffuse into the substrate. Thus, decrease of adhesion on increase of polarity of a polar adhesive must be considered a purely kinetic effect. If a nonpolar substrate were used instead of the polar cellophane, an increase in polarity of the adhesive would also decrease adhesion. This phenomenon would be differently explained: the increase of polarity of the adhesive would decrease its solubility in the nonpolar substrate, i.e., it could be explained on purely thermodynamic grounds.

It is worthwhile to note that increase in polarity does not always bring about decrease in adhesion. For example, McLaren^{8, 10} established that on increasing the chlorine content in chlorinated polyethylene the bond strength between the polymer and cellophane at first increased and then decreased. McLaren also observed that decreasing the amount of polar groups such as chlorine, carboxyl, carbonyl or hydroxyl may improve adhesion of the polymer to cellophane. This observation may be explained by the fact that at moderate polarity the increase of adhesion due to better solubility overshadows the decrease of adhesion due to deterioration of the diffusion ability of the adhesive. In conclusion, it may be stated that the diffusion theory explains well the effects observed in the technology of adhesives: the use of solvents common for adhesive and substrate, addition of plasticizers or fillers to the adhesive, rejuvenating of surfaces with solvent before bonding, etc. Such explanations may be found in a series of technical papers published recently³⁰.

SUMMARY

A theory of adhesion of polymers to each other is suggested; according to it adhesion of dissimilar polymers as well as auto-adhesion is explained by the diffusion of chainlike molecules segmentally or otherwise. Starting with this theory, the effects of various factors on the adhesion of polymers to each other are discussed. The factors considered are: duration of contact between adhesive and substrate, temperature, molecular weight of adhesive, molecular shape and polarity.

REFERENCES

- ¹ Hurd, C. B. and Mers, P. C., *J. Am. Chem. Soc.* **68**, 61 (1946).
- ² Bancroft, M. D., "Applied Colloid Chemistry" McGraw-Hill, N. Y. 1926, 81.
- ³ Hardy, W. B. and Nottage, M. E., *Proc. Roy. Soc.* **112**, 62 (1926); **118**, 209 (1929); *Phil. Trans.* **230** (1931).
- ⁴ Hardy, W. B., *Proc. Roy. Soc.* **138**, 259 (1932).
- ⁵ Nottage, M. E., *Proc. Roy. Soc.* **126**, 630 (1930).
- ⁶ McBain, J. W. and Lee, W. J., *Phys. Chem.* **31**, 1674 (1927); **32**, 1178 (1928); *Proc. Roy. Soc.* **113**, 606 (1927); *Ind. Eng. Chem.* **19**, 1005 (1927); *J. Soc. Chem. Ind.* **321**, 46 (1927).
- ⁷ DeBruyne, *Aircraft Engineering* **16**, 115, 140 (1944); *The Aircraft Engineer* **18**, 1, 947; *Materialkenntnis*, **1947**, 51.
- ⁸ McLaren, A. D., Hofrichter, C. H., *Paper Trade*, **125**, 19, 96 (1947).
- ⁹ Hofrichter, C. H. and McLaren, A. D., *Ind. Eng. Chem.* **40**, 329 (1948).
- ¹⁰ McLaren, A. D., *J. Polymer Sci.* **3**, 652 (1948).

- ¹¹ McLaren, A. D. and Seiler, C. I., *J. Polymer Sci.* **4**, 63 (1949).
- ¹² McLaren, A. D., Symposium "Adhesion and Adhesives", John Wiley and Sons, N. Y., 1954, p. 57.
- ¹³ A series of papers published in the symposium "Adhesion and Adhesives," John Wiley and Sons, N. Y., 1954.
- ¹⁴ Deryagin, B. V. and N. A. Krotova, "Adhesia", Akad. Nauk USSR, M.-L. 1949.
- ¹⁵ Deryagin, B. V., *Vestnik Akad. Nauk USSR* 1954, No. 7, p. 10.
- ¹⁶ Skinner, S. M., Savage, K. L. and Rutzler, D. E., *J. Appl. Phys.* **24**, 438 (1953).
- ¹⁷ Voyutskii, S. S., *Legkaya Promy.*, No. 1, 42 (1953).
- ¹⁸ Voyutskii, S. S., Shapovalova, A. I. and Pisarenko, A. P., *Dokl. Akad. Nauk USSR* **105**, 1000 (1955).
- ¹⁹ Shapovalova, A. I., Voyutskii, S. S. and Pisarenko, A. P., *Kolloid. Zhur.* **18**, 485 (1956).
- ²⁰ Voyutskii, S. S., Shapovalova, A. I. and Pisarenko, A. P., *Kolloid. Zhur.* **19**, 274 (1957).
- ²¹ Josefowitz, D. and Mark, H., *Ind. Rubber World*, **106**, 33 (1942).
- ²² Voyutskii, S. S. and Margolina, Iu. L., *Uspekhi Khim.* **18**, 449 (1949); *RUBBER CHEM. & TECHNOL.* **30**, 544 (1957).
- ²³ Voyutskii, S. S. and Shtarkh, B. V., *Dokl. Akad. Nauk USSR* **90**, 573 (1953); *Kolloid. Zhur.* **15**, 3 (1954); *RUBBER CHEM. & TECHNOL.* **30**, 548 (1957).
- ²⁴ Shapovalova, A. I., Tsvetkova, N. A., Voyutskii, S. S., *Nauchno-Issledovatel'skiye Trudy CNIKZ, sbornik V. Gilepprom*, M. 1953.
- ²⁵ Crishin, N. A., Voyutskii, S. S., Gudimov, M. M., *Dokl. Akad. Nauk USSR* **116**, 629 (1957).
- ²⁶ Deryagin, B. V., Zherobkov, S. K., Medvedeva, A. I., *Kolloid. Zhur.* **18**, 4 (1956).
- ²⁷ Alekseyenko, V. I., Mishutin, I. U., Voyutskii, S. S., *Dokl. Akad. Nauk USSR*, **95**, 93 (1954); *Kolloid. Zhur.* **17**, 3 (1955).
- ²⁸ Seiler, C. J., *Paper Trade J.* **126**, 37 (1928).
- ²⁹ See Sbornik "Prochnost svyazi mezhdu elementami rezino-tkanye & vykh izdelii v proizvodstve ekspluatatsii". Goskhimizdat M.-L. 1956.

ADHESION PHENOMENA IN THE BONDING OF RUBBER TO METAL BY MEANS OF LEIKONAT BONDING AGENT. 2. UNFILLED VULCANIZED RUBBER *

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In a previous communication¹ it was shown that the bond strength of unfilled vulcanized rubbers to metal by means of the isocyanate bonding agent Leikonat is high where the intensities of the interaction of the bonding film with the rubber and with the metal are approximately identical. As the experiments carried out at that time showed, the intensity of the interaction of the bonding film with the metal and the rubber is influenced by such factors as the character of the treatment of the surface of the metal, and also the form of filler incorporated in the rubber, which makes it possible to vary the bond strength of the rubber to the metal. The present paper deals with the investigation of adhesion phenomena in attaching unfilled rubbers to metal by means of Leikonat bonding agent.

According to the electrical theory of adhesion², the high figures for the work of pulling away films of polymers from hard backings are governed by the fact that on the boundary of contact of the polymer and backing there is formed an electrical double layer which acts as a type of condenser. The work done in pulling away the film from the backing is used in overcoming the force of attraction between the layers of the condenser with charges of different sign. As the layers are moved apart so the potential difference increases. The occurrence of an electrical discharge terminates the increase in the potential difference. Thus the work of pulling away a film from a backing depends upon the density of the charges of the electric double layer. In its turn the density of the charges is directly connected with the surface and volume properties of the contacting materials. We may suppose that the electrical double layer may be formed as a result of the following processes: a) of chemical reaction of the film with the backing, accompanied by a transition of electrons from one phase to another, on account of their donor and acceptor properties; b) of the different affinity for the electron of the two contacting surfaces; c) of the orientated adsorption of the dipole molecules of the film, at the interface. With this the occurrence of a dipole jump in potential at the interface of the two phases is responsible for a redistribution of the electrons between them, which is equivalent to the setting-up of a double electrical layer the layers of which are situated in both phases, and which consequently must separate when the contact is destroyed, in other words the dipole adsorption monolayer causes or strengthens different electron-affinities in the two contacting bodies.

The process of formation of bonds at the bonding agent-polymer and bonding agent-metal interface layers may take place according to different mech-

* Translated by R. J. Moseley, Research Association of British Rubber Manufacturers, from *Kolloid Zhur.* 21, 558-563 (1959).

anisms depending upon the composition, structure and properties of the contacting substances, and also upon the conditions under which the formation of the bonds takes place (temperature and pressure). In the case of bonding of vulcanized rubber to metal by the intermediary of a bonding interlayer high adhesion at the bonding agent film-polymer interface layer will be determined mainly by the composition and structure of the polymer. Apparently the higher the polarity of the rubber, the higher its adhesion properties will normally be. The high strength of the bond at the interface of polar rubber and backing is due to the fact that at this interface there takes place orientated adsorption of the molecules of the rubber. It is evident that in the case of a bond being created between a nonpolar rubber and backing orientated adhesion will play an insignificant role. In this case the formation of the double electrical layer is due to the forces of chemical interaction of the nonpolar rubber with the substance which is the base of the backing (the bonding agent).

In the light of the above it was interesting to investigate the nature of the forces causing the formation of a bond between vulcanized rubbers based on different polymers on their bonding to metal by the Leikonat cement which is extensively used as a bonding medium.

TABLE 1

Compounding ingredients	Reference numbers						
	A-1 Natural rubber	A-2 Nairit	A-3 SKS-30	A-4 SKN- 18	A-5 SKN- 26	A-6 SKN- 40	A-7 Butyl rubber
Rubber	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Magnesium oxide	—	7.0	—	—	—	—	—
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	0.5	—	2.0	0.5	0.5	0.5	3.0
Mercaptobenzothiazole	0.7	—	0.6	0.8	0.8	0.8	0.65
Tetramethylthiuram disulfide	—	—	0.1	—	—	—	1.30
Sulfur	3.0	—	2.0	1.5	1.5	1.5	2.0
Total	109.2	112.0	109.7	107.8	107.8	107.8	111.95
Vulcanization time at 143°, min	20	30	60	50	50	50	50

The investigation was carried out with unfilled vulcanized rubbers based on various polymers. The formula is given in Table 1, in parts by weight.

The vulcanized rubbers are secured with Leikonat bonding agent to a smooth metal plate (cleaned with No. 100 emery paper) during vulcanization. The bond strength is indicated by the resistance to stripping of the rubber from the metal and is expressed in kilograms per cm. of the width of the specimen (i.e., is expressed in units of work in relation to the unit of area, in erg/sq cm).

The results of preliminary tests show that in a number of cases the bond strength exceeds the strength of the vulcanized rubbers themselves and the break has a cohesive character. In order to get rupture in all cases of an adhesive nature when stripping the vulcanized rubber from the metal we reduced the thickness of the bonding agent film. It was nevertheless apparent that the reduction in the thickness of this film has a different effect upon the bond strength of vulcanizates of different polymers.

The results of the tests, presented in Table 2 and in Figure 1, provide evidence that by means of the bonding agent based on triisocyanato-triphenyl methane, it is possible to attach vulcanizates based either on polar or nonpolar rubbers to metal.

If we work along the line of increasing polarity of the polymers, we may imagine the following picture: there are no polar groups in the composition of

TABLE 2
INFLUENCE OF THICKNESS OF BONDING AGENT FILM UPON THE CHARACTER OF PULLING AWAY AND UPON THE STRIPPING RESISTANCE (KG/CM) OF VULCANIZED RUBBER FROM METAL

No. of vulcanizate	Thickness of film, μ									
	3.2*		1.6		0.4		0.2		0.1	
	kg/cm	Character of stripping	kg/cm	Character of stripping	kg/cm	Character of stripping	kg/cm	Character of stripping	kg/cm	Character of stripping
A-7 (butyl rubber)	0.4	Bonding agent remains on metal	0.1	Bonding agent remains on metal	—	—	0.1	Bonding agent remains on metal	—	—
A-1 (natural rubber)	4.68	do.	0.25	do.	0.16	Bonding agent remains on metal	—	—	—	—
A-3 (SKS-30)	1.46	Rubber breaks	0.65	do.	0.24	do.	—	—	—	—
A-4 (SKS-18)	3.94	Greater part of bonding agent remains on metal	3.07	do.	2.66	do.	2.24	Bonding agent remains on metal	2.20	Bonding agent remains on metal
A-2 (Nairit)	3.12	do.	2.98	do.	2.73	do.	—	—	1.40	do.
A-5 (SKN-26)	2.93	Part of bonding agent remains on metal	2.97	Greater part of bonding agent remains on metal	1.80	do.	—	—	1.46	do.
A-6 (SKN-40)	0.83	Bonding agent remains on rubber	1.02	Part of bonding agent remains on rubber, part on metal	1.03	Greater part of bonding agent remains on metal	—	—	1.01	do.
									0.68	Bonding agent remains on metal

* A bonding agent of thickness 3.2μ corresponds to Leikmat bonding agent of concentration 20%.

butyl rubber, and from the chemical aspect also it is less active, therefore when vulcanizates based on it are bonded to metal by means of Leikonat the bond strength is insignificant. On stripping the vulcanized rubber from the metal all the bonding agent remains on the metal. Natural rubber contains an insignificant number of polar groups, yet from the chemical aspect it is far more active than butyl. An unfilled vulcanizate of natural rubber bonds very well to metal by means of Leikonat. Nevertheless, in stripping the vulcanized rubber from metal the bonding agent remains on the metal, consequently the adhesion of the bonding agent to the metal is still higher than it is to the rubber. An unfilled vulcanizate of butadiene-styrene rubber also adheres very well to metal with Leikonat, so that the bond strength exceeds that of the rubber itself. Nevertheless, because of the low strength of the rubber itself the absolute magnitude of the work of stripping, which characterizes the bond strength of this rubber to the metal, is not high (1.47 kg/cm); during the testing of the specimens we were able to observe that the bonding agent remains on the metal. An unfilled vulcanizate of SKN-18 contains a definite number of polar groups and adheres well to metal with the help of Leikonat (but somewhat less well

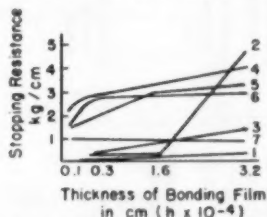


FIG. 1.—Influence of thickness of Leikonat bonding film upon the bond strength to metal of unfilled vulcanizates based on a series of raw rubbers: 1—Butyl rubber, 2—Natural rubber, 3—Butadiene-styrene, 4—SKN-18, 5—SKN-26, 6—Nairit, 7—SKN-40. Individual points have been omitted in this drawing.

than vulcanizates of natural rubber). On stripping from the metal a certain portion of the bonding agent is transferred from the metal to the vulcanized rubber. A vulcanizate of SKN-26 contains a greater number of polar nitrile groups than with SKN-18. This vulcanizate adheres to metal with Leikonat sufficiently well, but somewhat less strongly than an SKN-18 vulcanizate. On stripping from metal part of the bonding agent remains on the metal, but the greater part is transferred to the rubber. A Nairit (polychloroprene RJM) vulcanizate behaves similarly to an SKN-26 vulcanizate. An SKN-40 vulcanizate, containing the greatest number of polar groups, adheres weakly to metal with Leikonat bonding agent, and on stripping from the metal all the bonding agent is transferred to the vulcanized rubber.

Thus with the increasing chemical activity and polarity of the polymers we get an increase in the intensity of interaction of the bonding agent film with the vulcanizates, while the intensity of the interaction of the bonding agent film with the metal remains constant. Nevertheless, as the results show, in a given case the bond strength does not increase monotonically with increasing chemical activity and polarity of the polymers—it increases at first, passes through a maximum, and then falls. If we use the designations: A_1 —intensity of interaction of the bonding agent film with the vulcanized rubber, A_2 —intensity of interaction of the bonding agent film with the metal, then

1) where $A_1 < A_2$ the bond strength of the vulcanized rubber to the metal is poor. An example is the bonding to metal of a vulcanizate based on a chemically inert, nonpolar rubber, using Leikonat bonding agent (butyl rubber).

2) where $A_1 \approx A_2$ the bond strength of the vulcanized rubber to metal is good. An example is the bonding to metal of a vulcanizate based on a chemically active rubber or on a rubber with moderate polarity (natural rubber, SKS-30, SKN-18, Nairit, or SKN-26)

3) where $A_1 > A_2$ the bond strength of vulcanized rubber to metal is poor. An example is the bonding to metal of a vulcanizate based on a rubber containing the highest number of polar groups (SKN-40).

Thus it is evident that the bond strength of a vulcanizate to metal is high only in the case of approximate equality of intensity of interaction at the bonding agent—metal and bonding agent—rubber interfaces. If the intensity of interaction with one of the surfaces in contact with the bonding agent layer is significantly greater than with the other then the bond strength of the rubber to metal is low.

As has been shown¹ the intensity of a bonding agent film with a metal surface is increased by sand blasting the latter. Therefore if these vulcanized rubbers are bonded to a sand blasted metal surface, the whole picture alters.

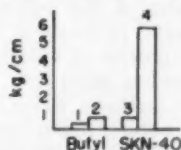


Fig. 2.—Influence of treatment of metal surface upon the bond strength of SKN-40 and butyl rubber vulcanizates to the metal surface: 1 and 3—metal cleaned with emery paper No. 100, 2 and 4—metal sand-blasted.

We selected the two most characteristic cases, the bonding of unfilled vulcanizates of butyl rubber and SKN-40. Both rubbers adhere poorly to a smooth metal surface, the butyl rubber because of weak adhesion at the bonding agent—rubber interface, and with SKN-40 because of weak adhesion at the bonding agent—metal interface. Sand blasting the metal has a different influence in each case on the bond strength of these rubbers to the metal (cf. Figure 2). While the bond strength of the butyl rubber vulcanizate to the sand blasted metal hardly changes (a certain increase in the bond strength takes place possibly as a result of the increase in the area of contact during sand blasting of the surface of the metal), the bond strength of the vulcanizate of SKN-40 increases approximately by a factor of 10, and further increase is limited by the strength of the vulcanized rubber itself, since the specimens break in the rubber.

As the test results shown in Table 2 and Figure 1 indicate, a reduction in the thickness of the bonding agent film has a varying influence upon the bond strength of vulcanizates based upon various polymers.

If we are following the alteration in the character of the separation from the data presented in Table 2, it may be remarked that a reduction in the thickness of the bonding agent film causes a reduction in the concentration of bonding agent, and this in its turn causes the intensity of interaction on the bonding agent with the vulcanized rubber to be lowered. This is shown in the course of the curve illustrating the dependence of the bond strength of the rubber to the metal upon the thickness of the bonding agent film. If we use the designations A_1 —intensity of interaction of a film of undiluted bonding agent with vulcanized rubber; A'_1 —intensity of interaction of a film of diluted bonding agent with vulcanized rubber; and A_2 —the intensity of interaction of a film of bonding agent with the metal, then the experimental data indicate that with dilution of the bonding agent $A'_1 < A_1$ (a general rule).

For vulcanizates of nonpolar rubbers.—For undiluted bonding agent $A_1 \leq A_2$. For a diluted bonding agent $A'_1 \ll A_2$ (with dilution of the bonding agent the bond strength falls sharply).

For vulcanizates of SKN-18, Nairit and SKN-26, polymers of medium polarity.—For undiluted bonding agent $A_1 \geq A_2$. For a diluted bonding agent $A'_1 \approx A_2$ (with dilution of the bonding agent the bond strength falls very slowly).

For vulcanizates of SKN-40 (a highly polar rubber).—For undiluted bonding agent $A_1 \gg A_2$. For a diluted bonding agent $A'_1 \geq A_2$ (with dilution of the bonding agent the bond strength increases slightly).

Using Leikonat bonding agent it is possible to bond to metal sufficiently strongly vulcanizates based either on polar rubbers or on chemically active nonpolar rubbers (natural rubber, SKS-30). In the process of formation of a bond at the bonding agent-rubber interface the polar groups take an active part, which may be seen from the example of the adhesion of unfilled vulcanizates and raw rubbers (SKN-18, SKN-26 and SKN-40). The higher the content of nitrile groups in the polymer the higher the intensity of interaction of the bonding agent film with vulcanizates of this polymer. In bonding compounds based on nonpolar rubbers to metal by means of Leikonat bonding agent there may apparently occur (in the process of vulcanization), a chemical reaction between the rubber and the bonding agent film.

Since triisocyanatotriphenyl methane, which is the basis of Leikonat bonding agent, is polyfunctional by nature, it can interact simultaneously not only with one molecule of the raw rubber but with several, which leads to a process of formation of a structural network similar to that occurring in vulcanization. To test this suggestion it was thought desirable to investigate the interaction of raw rubber with isocyanate in solutions and to investigate the action of isocyanate as a vulcanizing agent.

CONCLUSIONS

1. The bond strength of vulcanized rubber to metal brought about by means of a bonding agent film is regulated by the ratio of the intensities of interaction of the bonding agent film with the contacting surfaces at the bonding agent-rubber and bonding agent-metal interfaces. Where these are approximately equal the bond strength is greatest. Where they differ sharply the bond strength decreases.

2. One of the factors influencing the intensity of interaction of a bonding agent film with vulcanized rubber is a reduction in the thickness of the bonding agent film; with reduction in the thickness of the bonding agent film the intensity of interaction of the bonding agent with the vulcanized rubber falls; this is expressed in varying ways in the bond strength to metal of vulcanizates of various rubbers, causing a fall-off in some cases, and in some other cases a certain increase in the bond strength of the vulcanized rubber to the metal.

3. By means of the Leikonat bonding agent it is possible to bond unfilled vulcanizates based on the majority of existing polymers, whether polar or nonpolar, to metal sufficiently strongly.

4. It is established that on increasing the number of polar groups in the polymer there is an increase in the intensity of interaction of the bonding agent film with the vulcanizate containing that rubber.

REFERENCES

- ¹ Medvedeva, A. M., and Deryagin, B. V. and Zhrebkov, S. K., *Koll. Zh.*, **19**, 412 (1957).
- ² Deryagin, B. V. and Krotova, N. A., "Adhesion", *Izd. AN SSSR*, 1949.

TEMPERATURE DEPENDENCE OF THE MECHANICAL AND STRESS-OPTICAL BEHAVIOR OF ELASTOMERS *

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INTRODUCTION

Our purpose was to carry out a precise experimental investigation of the temperature dependence of the modulus of elasticity and of the stress-optical constants of elastomers. For this purpose we had constructed to our specifications a very accurate measuring apparatus with which we could make mechanical-optical measurements on a whole series of different elastomers.

If our measurements had given a clear verification of the predictions from theory made in the earlier work of Müller¹ and of Kuhn and Gr \ddot{u} n², we could then have confined our paper to a brief report of the experimental data. Then too, we probably would have had the opportunity to describe more accurately the dependence on constitution of the stress-optical constants in the light of those theories, which is what we originally had in mind. We find, however, that there are more or less clearly defined deviations between the experimentally determined temperature functions and the regularities which are derived from the theories. These differences seem to us to be extremely interesting, and we believe that we may be able to learn from them some important hints on molecular behavior in elastomers.

In formal analogy to gases, we can speak of "ideal" and "real" elastomers. In both cases forces between molecules, or within the molecules, bring about deviations from the "ideal".

We will first present an accurate description of the experiments and then try to explain the measurements from a theoretical point of view.

APPARATUS AND MEASURING TECHNIQUE

A rod-shaped test specimen is loaded with a freely hanging weight (see Figure 1), and the following measurements are made:

1. Thickness of testpiece
2. Width of testpiece
3. Distance between elongation marks
4. Load
5. Optical path difference
6. Test temperature

These values are measured at a series of loads up to an elongation of about 100%, at a constant temperature. The testpiece is mounted in a double-walled housing. The space between the walls is kept at a constant temperature by warm water which is held at the required temperature by a thermostat. A

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Kautschuk und Gummi*, Volume 12, No. 4, pages WT 83 to 95, April 1959.

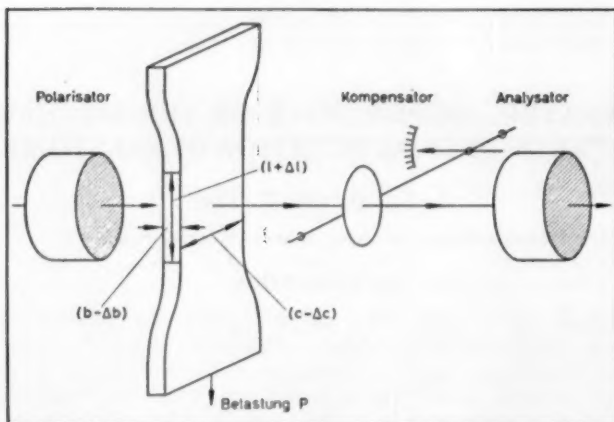


FIG. 1.—Arrangement of the testpiece. (Polarisator = Polariser; Kompensator = Compensator; Analysator = Analyzer; Belastung P = Load P).

mercury thermometer measures the temperature directly beside the sample (see Figure 2). The testpiece is located in the light path of a polarizing microscope, which is fitted with a low power objective which has a large object distance. The light of the microscope lamp is passed through a water cell in order to avoid



FIG. 2.—Interior of the double walled chamber with the testpiece and mercury thermometer beside it.

local heating of the testpiece. The front wall of the case is a removable double window of plate glass through which the measurements of the elongation and thickness of the sample are made. A separate measuring microscope movable in two perpendicular directions is used for this purpose. The optical axis can thus be moved parallel to itself. The perpendicular movements can be accurately determined on a scale which is equipped with a lens. The apparatus (see Figure 3) enables the mechanical and optical measurements to be made very accurately.

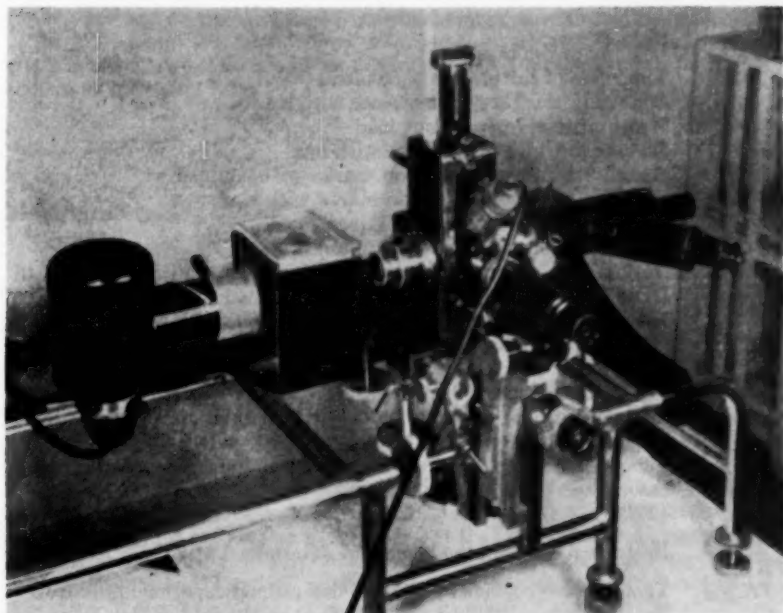


Fig. 3.—Assembled apparatus for the mechanical-optical measurement of rubber specimens.

The test specimens were vulcanized in polished steel molds in the form of transparent sheets of 1 mm thickness and later rods 5 mm wide were stamped from the sheets. The elongation marks were likewise 5 mm apart.

It is known that measurements of deformation processes in elastomers become constant only after a certain number of deformation cycles. We have noted this phenomenon in previous work. For this reason, we stretched the testpiece twenty times before the start of the measurements. The prestretching elongations were up to about 100%, which was also the value attained in the measurements. The pretreatment was done at room temperature.

The measurements were started at the lowest temperature which was to be used and the elongation was increased by seven steps to a final value of about 100%. The measurements were made on the same samples without changing the clamps for the whole temperature range. In addition to the force-elongation measurements, the thickness was determined at room temperature, and in addition—using a separate Abbé refractometer—the refractive index n_D was

determined over the whole temperature range. The temperatures used ranged between about 10° and 90° C; in several exceptional cases, certain vulcanizates of natural and synthetic rubbers were tested at temperatures up to about 140° C. On the basis of the measurements we could tell that a very decided material change took place rapidly in the test specimen above 90° C. This was, however, not a matter for our present research. The measurements were therefore carried out and reported up to a maximum temperature of about 90° C.

SYMBOLS AND DEFINITIONS

Symbols.—The following symbols are used in this work:

P	Loading of the testpiece
b	Thickness of testpiece without load
Δb	Change in thickness of testpiece with load
c	Width of testpiece without load
Δc	Change in width of testpiece with load
l	Distance between elongation marks without load
$l + \Delta l$	Distance between elongation marks with load
K_1	Stress-optical constant (See Equation 4)
K_2	Modulus of elasticity (See Equation 2)
Γ	Optical path difference for the test piece with load P
$(n_1 - n_2)$	Double refraction of the testpiece under load P
n_D	Normal optical refractive index of the unstretched material for the sodium D line
t	Test temperature on Centrigade scale
T	Test temperature on Kelvin scale
a_2	Temperature coefficient of the elastic modulus for "ideal" rubber (Equation 7)
$(TK)_{K_2}$	Temperature coefficient of the elastic modulus as experimentally determined
Δa_2	$(TK)_{K_2} - a_2$
$\left[\frac{1}{K_1} \right]_{20}$	Reciprocal stress-optical constant determined at 20° C
$[TK]_{1/K_1}$	Temperature coefficient of $1/K_1$ determined experimentally
a_1	Temperature coefficient for $1/K_1$ for "ideal" rubber (see Equation 11)
Δa_1	$[TK]_{1/K_1} - a_1$
$(\alpha_1 - \alpha_2)$	Anisotropy of the polarizability of the "mobile molecular parts"
k'	Boltzmann constant

Definitions.—1. Modulus of elasticity. A linear relation holds between stress and elongation when the elongation of an elastomer is not too high. The proportionality factor is known as the modulus of elasticity. To evaluate this factor, we could measure the stress when the elongation $\Delta l/l = 1$ (this corresponds to an elongation of 100%). This stress is then the same as the elastic modulus. We must understand that the stress is identical with the load per unit cross section. Hence the cross section must be measured under load. Herein lies a difference from the usual stress measurements, which are ordinarily based on the original value of the cross section before loading. The results of measurements here under consideration agree well with Equation (1)

$$\frac{P}{(b - \Delta b)(c - \Delta c)} = K_2 \cdot \frac{\Delta l}{l} \quad (1)$$

In the case of materials such as metals and low molecular weight solids, which have a very slight extensibility compared to rubber, we can disregard any reduction in cross section which accompanies the stretching and we can put the original cross section ($b \cdot c$) in Equation (1) in place of the cross section under load $(b - \Delta b)(c - \Delta c)$. As can be seen we then have Hooke's Law as it is known in mechanics.

In our measurements, we found that the thickness of the testpiece under load was the value which was measurable with the least degree of accuracy. It is probable that this thickness is not uniform throughout. Only the thickness of the edge was accessible for our measurements of thickness.

In order to get around this inaccuracy we have postulated constant volume and put the change of cross section as a function of elongation into Equation (1) to give us Equation (2).

$$\frac{P}{b \cdot c} = K_2 \cdot \frac{\Delta l}{l + \Delta l} \quad (2)$$

Moreover, Equation (3) holds for $\frac{\Delta l}{l}$:

$$\frac{\Delta l}{l} = \frac{P}{K_2 \cdot b \cdot c - P} \quad (3)$$

Equation (2) is also identical with Hooke's Law for very small extensions. Then we have $\frac{\Delta l}{l} \cong \frac{\Delta l}{l + \Delta l}$ and for small elongations $\frac{P}{b \cdot c} = K_2 \frac{\Delta l}{l}$ (Hooke's Law).

The value for the elastic modulus given in the following is the calculated value of K_2 obtained by putting our test data in Equation (2).

The various elastomers which we studied followed quite closely the behavior indicated by Equations (1) and (2), but not exactly. The trivial deviations show up for the greater part in the fact that the value of K_2 comes out a bit high in the region of very small elongations, $\Delta l/l$ about 0.1 to 0.2. In general, Equations (1) and (2) apply up to elongation values of $\Delta l/l = 1$ to 1.5. From our observations, only very heavily crosslinked vulcanizates show any particular deviations for elongation values below l .

2. Stress-optical constant. In both of the investigations of the stress-double refraction relationship cited above, by Müller¹ as well as by Kuhn and Gr \ddot{u} n², the quotient of double refraction divided by stress is considered to be a material constant. It is called the stress-optical constant; it is dependent on temperature and we identify it as K_1 :

$$K_1 = \frac{(n_1 - n_2)(b - \Delta b)(c - \Delta c)}{P} = \frac{\Gamma(c - \Delta c)}{P} \quad (4)$$

Furthermore, Equation (5) applies for $(n_1 - n_2)$ and then Equation (6) is obtained by substitution in Equation (4):

$$(n_1 - n_2) = \frac{\Gamma}{(b - \Delta b)} \quad (5)$$

$$\frac{P}{(c - \Delta c)} = \frac{1}{K_1} \cdot \Gamma \quad (6)$$

TABLE I
MECHANICAL AND STRESS-OPTICAL MEASUREMENTS FOR VARIOUS ELASTOMERS

Identifi- cation	Cure min./° C	Type of rubber	$\left(\frac{1}{K_1}\right)_{10}$ kg cm ²	$\left[\frac{TK}{K_1}\right]_{10}$ Experimental	$\frac{a_1}{g}$ "ideal" cm ³ deg.	Δa_1	$(K_2)_{10}$ kg cm ²	$\frac{a_2}{g}$ $\frac{(TK)_{10}}{\text{Experimental}}$ cm ³ deg.	Δa_2	$\frac{a_2}{g}$ for 20° C	(TK) _{-p}	Density at 22° C
Vulkollan												
A 17	60/143°	Buna S III Heat softened	5 850	12.6	21.4	-8.8	45.7	-89	156	-245	1.5048	1.245
A 26	60/143°	Neoprene RT	5 360	20.0	20.1	-0.1	21.0	24	72	-48	-0.00034	1.052
Oppanol	—		4 540	15.1	17.2	-2.1	13.5	11	46	-35	-0.00032	1.265
A 34	60/143°	Oppanol B200	6 130	20.0	22.4	-2.4	5.6	-10	19	-29	0.00030	0.916
		Nat. rubber	3 975	11.1	15.1	-4.0	11.6	14	40	-26	-0.00039	0.932
		Defo. ca. 250										
A 27	60/143°	Perbunan	3 380	14.9	12.7	2.2	19.7	43	67	-24	-0.00032	0.984
A 32	60/143°	Polyzar SX 371	4 715	17.3	17.6	-0.3	16.9	34	58	-24	-0.00034	0.971
A 11	60/143°	Nat. rubber	4 150	9.9	15.7	-5.8	14.4	31	49	-18	-0.00036	0.957
A 37	60/143°	Coral rubber	3 940	9.5	14.7	-5.2	9.9	18	34	-16	-0.00036	0.942
A 16	60/143°	Buna S III crude	4 015	17.8	15.3	2.5	19.9	58	68	-10	-0.00034	0.982
A 35	—	Silicone rubber	74 500	-490.0	250.0	-740.0	1.8	0	6	-6	-0.00036	1.002
A 1	20/143°	Nat. rubber	4 650	8.3	17.0	-8.7	17.8	55	61	-6	-0.00037	0.945
A 30	60/143°	Cold rubber SBR 1500	3 520	19.0	13.4	5.6	14.4	53	49	4	-0.00039	0.980
A 36	60/143°	Polybutadiene	3 310	17.9	12.7	5.2	28.4	124	97	27	-0.00037	0.935

Additional Information for Table I.

Vulkollan

Prepared from 100 parts by weight of Desmophen 2000 and 18 parts Desmodur 15. Cross-linked with 2 parts butane-diol; mixed at 120° C; condensation finished at 115° C.

Sulfur

Cure: 60 min/143° C

2.

A 17. Buna S III. Heat Softened

Buna S III. Heat softened.
Defo 500 100.
Zinc oxide, active 2.
Vulkacit CZ 1.
Sulfur 2.
Cure: 60 min/143° C

A 26. Neoprene RT

Neoprene RT 100.
Zinc oxide, active 3.
Cure: 60 min/143° C

Oppanol B200

The test specimen of Oppanol B200 was heated in a mold for 30 min. at 191° C. The mold was cooled under pressure and the sample then removed. Because of its nature, this material was tested only up to 70° C.

A 34. Natural rubber, heavily milled

First Latex Crepe; Defo about 250 100.
Zinc oxide, active 2.
Vulkacit CZ 1.25
Sulfur 3.75
Cure: 60 min/143° C

A 27. Perbunan

Perbunan 100.
Zinc oxide, active 2.
Vulkacit CZ 1.
Sulfur 2.
Cure: 60 min/143° C

A 32. Polysar SX 371 (butadiene/styrene copolymer, crosslinked with divinyl benzene)
Polysar SX 371 100.
Zinc oxide, active 2.
Vulkacit CZ 1.

A 11. Natural rubber

First Latex Crepe, crude 100.
Zinc oxide, active 2.
Vulkacit CZ 1.25
Sulfur 3.75
Cure: 60 min/143° C

A 37. Coral rubber

Coral rubber 100.
Zinc oxide, active 2.
Vulkacit CZ 1.25
Sulfur 3.75
Cure: 60 min/143° C

A 16. Buna S III, crude

Buna S III, crude 100.
Zinc oxide, active 2.
Vulkacit CZ 1.
Sulfur 2.
Cure: 60 min/143° C

A 35. Silicone rubber

Siloprene (Wacker); (Silicone rubber as a viscous liquid) 100.
Peroxide paste (Wacker) 2.
Aerosil 5.

A 1. Natural rubber

First Latex Crepe, crude 100.
Zinc oxide, active 2.
Vulkacit CZ 1.25
Sulfur 2.50
Cure: 20 min/143° C

A 30. Cold rubber

Cold rubber, SBR 1500 100.
Zinc oxide, active 2.
Vulkacit CZ 1.
Sulfur 2.
Cure: 60 min/143° C

A 36. Polybutadiene

Polybutadiene 100.
Hycar 1312 } Very lightly milled 2.
First Latex Crepe } as plasticizer 2.
Zinc oxide, active } 2.
Vulkacit CZ 1.
Sulfur 2.
Cure: 60 min/143° C

Equation (6) is found to be especially good for showing the results of the measurements. It is astonishing how accurately all of the elastomers which we studied follow this equation. In some cases, the straight line drawn through the points indicating measured values does not pass through the zero point. In such cases, we have represented K_1 by the value of the slope of the line.

To sum up, it is to be noted that the numerical values of the material constants K_1 and K_2 for each temperature used were obtained by plotting six or seven pairs of values in the way defined by Equations (2) and (4).

K_1 = Stress-optical constant (double refraction at the reciprocal stress 1), dimensions cm^2/kg and K_2 = Modulus of elasticity (stress calculated for the loaded cross section when the elongation $\Delta l/l = 1$), dimension kg/cm^2 .

TEMPERATURE DEPENDENCE OF THE MODULUS OF ELASTICITY

Meyer and Ferri³, Kuhn⁴, Müller¹, Kuhn and Grün² and other authors postulate for elastomers a direct linear relation between the elastic modulus and absolute temperature. This formulation, as has been indicated, is tied in with certain simple assumptions: for example, Müller points out that the required direct proportionality (see Equation 7) is to be expected only in certain favorable cases, such as, for instance, when an irreversible sliding of the molecules (macro-Brownian movement, according to Kuhn)—and thus a plastic deformation—is eliminated and also the crosslink density is not too high. Our results verify this, but they also let us surmise that other conditions enter the picture. According to the simple assumptions upon which we have touched, and which we will discuss further in connection with the interpretation of the results, the modulus of elasticity, K_2 , according to the theory of Kuhn and of Müller, varies in direct proportion to the absolute temperature, T (see Equation 7), or with the temperature, t , in the more familiar Centigrade scale (see Equation 8). Equations (7) and (8) hold true only in the temperature range of rubber elasticity.

$$(K_2)_T = a_2 T \quad (7)$$

$$(K_2)_t = (K_2)_{20} \cdot \frac{273 + t}{293} \quad (8)$$

Our measurements have shown that the temperature function of the modulus of elasticity is practically linear for all the elastomers tested in the temperature range from about 10° C to about 90° C. But the slopes of the lines show a more or less significant positive or negative deviation from the theoretical value $(K_2)_{20}/293$ (Equation 8) when the value of K_2 at 20° C is used as the point of reference, which we did.

According to theory, the temperature coefficient (slope of the lines) would be determined solely by the value of the modulus of elasticity at one reference temperature. In Table I, we have assembled the temperature coefficients determined by experiments as well as the values of $(K_2)_{20}$ and the theoretical values of a_2 as calculated from Equation (7). Also in Table I are given the deviations mentioned, that is the difference between the measured and the calculated values of a_2 . These deviations are given under Δa_2 . For the sake of a better overall view, Table I also contains the measurements for the density and the refractive index and its temperature coefficient, as well as the data from the stress-optical measurements, which we will go into more thoroughly later.

The "measured temperature coefficients" given in Table I were derived as follows: The value of K_2 (elastic modulus) for each temperature was determined by graphic interpolation. The values of K_2 thus obtained are plotted against the temperatures and the points joined by a straight line (using the method of least squares). The slope of the calculated straight line gives the "measured temperature coefficient". This procedure assumes that the dependence sought can be represented at least approximately as a linear relationship in the chosen temperature range. This is actually the case both according to theory and experiment.

Natural rubber was given certain special handling in some of our work. Thus, we tested this elastomer in a variety of compounds, and studied thoroughly the effect of vulcanization time and temperature. The measurements are given in Table III. In Table I, however, are given the various synthetic and natural vulcanizates which were cured under comparable conditions.

INTERPRETATION OF THE EXPERIMENTAL RESULTS

Temperature dependence of the elastic modulus.—The relationship formulated by Equations (7) and (8) rests upon a series of idealized or highly simplified assumptions. Thus, the individual thermal movement of the units (segments) of the chain molecules must be free and unhindered in all three dimensions. Another assumption is that the chain units as such must not change in their structure in the temperature range used. That would mean that no change in the primary and secondary valence bonds take place. Finally, as has already been indirectly indicated and as Müller¹ has pointed out, the mesh width in the molecular network must not change. Hence, all points of attachment in the network due to primary valences, as well as all those due to hook, loops, and adhesions must remain stable in the temperature range used.

So, according to theory (Equations (7) and (8)), we must assume a molecular network which remains constant in its general structure with change of temperature. The only permissible change with rising temperature should be a more intense thermal agitation of the chain units. An elastomer which satisfied these rigorous conditions is an "ideal" rubber. Naturally, this does not mean that such a rubber—if there be any—deserves to be called "ideal" with respect to its technological properties.

Before we look more closely into the irregular structure of "real" rubber, we would like to speak about the nature of rubber elasticity in order to get a better understanding of more recent statements about the concept of "ideal" rubber. The present day, generally accepted interpretation of rubber elasticity is based on ideas advanced by Meyer, von Susich and Valko⁵, and later developed further by Kuhn⁶, by Guth and Mark⁷, as well as by Müller¹ and other authors.

As has been previously stated, the long chain of the rubber molecule can, in the ideal case, move about in such ways that every chain unit can move freely and unhindered in any conceivable direction. Because of the unrestrained mobility on the one hand and the random thermal agitation on the other, the filamentary molecule can assume any configuration from the completely tangled or coiled to the fully extended form. According to the laws of statistics, all configurations are equally entitled to occur, but are not of the same probability. The arrangement which will be most frequently found will then be somewhere between the two extremes, and is called the "most probable coiled form". Thermodynamically expressed: the "most probable coiled form"

corresponds to the highest entropy value. With the application of a directed external force—for example, a pull—the filamentary molecule stretches (uncoils) in the direction of the force. The thermal agitation, however, endeavors to reestablish the most probable state and sets up a resisting force, an elastic restoring force, which increases with increasing elongation and finally becomes equal to the deforming force. After the force equilibrium is established, the process of stretching stops. The stresses put into the material cause a springing back after the load has been removed. Following these ideas, it is quite clear that the force required to cause a certain elongation must increase with increasing temperature, because the thermal agitation becomes stronger and the restoring forces arising from that agitation increase. The phenomena characteristic of elastic deformation of elastomers are thus explained through pure entropy effects.

This idealized limiting case of the pure entropy-elasticity is, as we know, a fiction and can be only more or less closely approached by "real" elastomers. Between the individual molecules of every elastomer are found specific reciprocal effects which can have their origin in secondary valence forces of all kinds or in steric hindrances. They affect the picture of the deformation—mechanical properties of the elastomer in a variety of ways. It would exceed the scope of this work to go more deeply into this subject. We only wish to discuss the question which is of special interest to us: How can we explain the differences between "theoretical" and experimentally determined temperature coefficients of the elastic modulus with the help of the intermolecular and intramolecular interactions? Through the appearance of these interactions, be they from attractive forces and/or steric hindrances, such as from bulky side groups, there arise bonding mechanisms between the molecules which, depending upon their intensity and number, bring about a more or less well defined elevation of the elastic modulus, because of the fact that the loosening of these bonding mechanisms upon stretching of the elastomer requires additional forces. The modulus of elasticity of "real" elastomers will not increase as sharply with rising temperatures as will the modulus of elastomers with pure entropy elasticity; for the bonds are weakened or destroyed by the increased thermal agitation, that is to say that the portion of the modulus which originates from the interaction forces diminishes with rising temperature. This has the same significance as reduction of the temperature coefficient of the elastic modulus.

Most of the elastomer types which are used in practice are crosslinked. By crosslinking we generally understand a primary valence bridging between the chain molecules of the elastomer. The elastic modulus increases with a rise in degree of crosslinking, which seems understandable. As long as the degree of crosslinking is not too high, that is, if the chains between points of attachment are long enough so that there is freedom of movement, the concepts here pictured about the molecular mechanism of high elasticity can be used in connection with this "wide-meshed network". If we consider the dependence on temperature of the elastic modulus from this point of view, then perhaps we can interpret the differences between the theoretical and experimental temperature coefficients more clearly as follows:

A "real" crosslinked elastomer contains two types of crosslinks, which we will call primary crosslinks (primary valence bonds) and secondary crosslinks (points of adhesion for secondary valence forces and/or bulky molecular groups). The primary links are heat stable in the temperature range used but the secondary links, on the other hand, are weakened or "melted" by rising temperatures and thus are unstable. In other words: the degree of crosslinking is diminished

by the destruction or weakening of the secondary crosslinks when the temperature rises. As a consequence, that part of the modulus which depends on these points of attachment is reduced in value. The temperature coefficient however does not become negative, because the part of the modulus which depends on the entropy mechanism of the wide-meshed network (with primary crosslinks) is larger and increases rapidly with rise in temperature. With real elastomers, according to this view, there results a positive but smaller temperature coefficient than in the case of "ideal" elastomers. Only Vulkollan shows a slight negative temperature coefficient. This means that the "energetic" portion of the modulus is reduced more rapidly than the entropy component is increased with rising temperature. Oppanol, an uncrosslinked thermoplastic elastomer also has a negative temperature coefficient.

We also perceive from the measurements that the "measured temperature coefficient" can be larger than that given by theory. This deviation in the positive direction is not explained by the previous considerations. In view of the many possible variations in the chemical structure and morphology of the elastomer molecules in question—we are speaking of natural rubber (in a particular recipe), polybutadiene and butadiene/styrene copolymers—it will be difficult to find a uniform explanation for this positive deviation of the temperature coefficient. In natural rubber there exists a symmetrical, strictly linear, chain molecule with the *cis* configuration while in the copolymers of butadiene and styrene, partly because of phenyl side groups and partly because of *trans* configuration and of 1,2-addition in the butadiene units, we have a very irregular bulky molecular structure. Then too, the polybutadiene which we used was peculiar in that it came from a laboratory preparation which was made at a relatively high temperature by an emulsion polymerization which was carried to a high conversion. This gave a product that showed but little plasticity in the unvulcanized state and vulcanized to an elastic but brittle material which had all the appearance of a highly crosslinked elastomer. The results of experiments show that the more bulky the elastomer's molecular structure, the greater is the positive deviation.

The natural rubber molecule, the classic representative of the linear highly flexible chain molecule, shows the smallest deviation from the "ideal" value of the temperature coefficient. It shows only a trivial difference from zero. After all, it is known that natural rubber can partially crystallize at lower temperatures and especially at higher elongations.

In extending the previously formulated explanation for the negative deviation of the temperature coefficient of the elastic modulus, it is quite conceivable that in the case of especially symmetrical elastomeric structures, not only individual intermolecular points of cohesion appear, but that whole molecular fragments cling to each other over a finite range. The aggregation is not thought of as being so extensive that the mobility of the chain molecules is greatly changed. These "super-structures" are weakened or destroyed by rising temperature so that the number of chain molecules increases, which would mean a rise in the modulus of elasticity, according to the theory of rubber elasticity.

In the case of elastomer types with bulky and asymmetrical structures and which show a positive deviation of the temperature coefficient, other phenomena must certainly be considered as causes of the deviation. It is conceivable, for instance, that at lower temperatures, the bulk/side groups and branches may block large sections of the chain, like meshed gear teeth, so that they cannot take part in the rubbery elastic deformation. Increasing tempera-

ture, by raising the thermal mobility will bring about successive loosening of the blocked portions; an elevation of the modulus of elasticity results.

A partial broadening and strengthening of the explanation attempted here for the positive deviation of the temperature coefficient from the theoretical value can be derived from the temperature function of stress-double refraction. It is therefore appropriate to interrupt these reflections and to go ahead with the reporting of our results of stress-optical measurements.

Temperature dependence of the stress-optical constants.—According to present ideas, the occurrence of double refraction in an elongated elastomer can be thought of as follows: When a beam of light penetrates matter, the atoms involved are subjected to the influence of an alternating electromagnetic field. Since each atom has its own positive and negative electrical charges, they will be affected by the external field, and a shift of the charge within the atom, or polarization will take place. It is understandable that the electrical charges in the atom and especially the structure of the electron shells can exert an effect on the polarizability. The nuclear charge number and indirectly the atomic weight influence the polarizability.

The occurrence of a refraction is at present explained by the supposition that every atom of the substance which is penetrated by the light is excited to vibrate because of its polarizability. According to the Huyghens' concept, it becomes a wave center⁸. All the atoms which are excited by the light waves then send out waves which interact with the energizing waves in such a way that in general the resultant light waves travel a little slower than light in a vacuum. The speed of propagation of the resulting vibration—or, what is most closely connected thereto—the refractive index of the substance under study, is very strongly affected by the way that the individual atoms can vibrate optically.

The charge displacements in molecules will depend not only upon the kind and strength of the individual atomic fields of force, but will also be significantly influenced by the type of bonding.

An example may clarify this interdependence. Consider the vibration possibilities of the electrons which are in a long filamentary molecule. It is clear that the possibilities of vibration are not the same in all directions. The long molecule is held together lengthwise by strong electrical forces but in the perpendicular direction—depending upon the composition—weaker forces in general are effective. The polarizability is therefore dependent upon orientation or is anisotropic.

The molecular chain—considered alone—is also strongly optically anisotropic, but it depends upon the cooperation of the many molecular chains in a macroscopic test specimen, whether the anisotropy of the individual filamentary molecules is outwardly apparent. As long as the filamentary molecules are arranged in completely random manner, the anisotropies of the individual molecular parts mutually neutralize each other and the specimen is isotropic in the aggregate. From the preceding section, it is assumed that the filamentary molecules of an elastomer due to thermal agitation arrange themselves in such ways that the highest degree of disorder is always reached. A piece of rubber under these conditions could be completely relaxed inwardly and outwardly. Then the double refraction is nil.

In the case where the molecular segments of the test sample are oriented by elongation, anisotropy will be found in increasing proportion by the optical measurements. Müller¹ made the great contribution of being the first to recognize the fact that the reason for the simple linear relation between stress

and double refraction, which had previously been demonstrated, is found in the fact that both effects stem from the same mechanism: the orientation of the molecules. This causes the stress as well as the double refraction. Our experiments have repeatedly shown that the linear relation can be recognized with unusual accuracy in measurements on rubber. So, if the double refraction which is found in stress-optical deformation tests is to be thought of as a measure for the statistical orientation of the molecular parts, then, on the other hand, the product of double refraction by the effective cross section must be proportional to the force for every deformation. Experiments justify this assertion. Of course, it is presumed that the mobile molecular segments remain unchanged in their "constitution" (including close packing) during the individual deformation tests. Comparable conclusions about the degree of orientation in a given elastomer can naturally be reached only under similar test conditions (over all physical pretreatment). The shape and dimensions of the test sample belong in this category. The relation between the force and the double refraction is expressed by the fundamental stress-optical Equation (9), which is derived from Equation (4).

$$(n_1 - n_2)(b - \Delta b)(c - \Delta c) = K_1 P \quad (9)$$

This relation becomes clearer when it is transposed, thus:

$$\frac{P}{(b - \Delta b)(c - \Delta c)} = \frac{1}{K_1} \cdot (n_1 - n_2) \quad (10)$$

Equation (10) corresponds exactly to the stress-elongation Equation (1), except that the double refraction $(n_1 - n_2)$ occurs in place of the elongation and the reciprocal stress-optical constant $1/K_1$ is found instead of the elastic modulus K_2 . The physical significance of the value $1/K_1$ appears simply as a modulus per unit of the double refraction. The analogy between K_2 and $1/K_1$ goes farther yet. It extends to the proportionality of the two moduli (elongation-modulus, K_2 and "double refraction modulus", $1/K_1$) to the absolute temperature (Equation 11).

$$\left(\frac{1}{K_1}\right)_T \cong a_1 T \quad (11)$$

$$a_1 = a' \cdot \frac{n}{(n^2 + 2)^2}$$

This relation holds true only for the ideal case. It is obtained by substituting the constant a_1 from the corresponding equations of Müller and of Kuhn and Gr \ddot{u} n \ddot{u} s. In using Equation (11) consideration must naturally be given to the temperature dependence of the index of optical refraction n_D .

In our work we have calculated the values of the theoretically valid temperature coefficient a_1 on the basis of values of $1/K_1$ for a reference temperature of 20° C for each of the elastomers, and have given these values in Tables I and II. The temperature coefficient $[TK]_{K_2}$ as found experimentally as well as the difference between it and its theoretical value, are also included in Tables I and II.

The analogy between Equations (1) and (10) has been explained in the foregoing considerations in such a manner that the orientation of the filamen-

tary segments is to be thought of as the same elementary molecular process not only in elongation but also with respect to stress double refraction.

In a given elastomer system the force necessary to bring about a predetermined elongation is dependent to a large extent upon the mesh-width of the network (crosslinking). On the other hand, the force needed to bring about a certain double refraction is practically independent of the crosslinking. This is verified by the well known fact that the elastic modulus (K_2) of products made from natural and synthetic rubbers depends greatly upon the state of vulcanization. The stress-optical constant, on the other hand, at least in the "ideal" case, is independent of the state of vulcanization. The effects of vulcanization on the stress-optical constant for natural rubber will be fully treated in the last section.

This difference indicates that in addition to the simple elementary process of segment-orientation, other processes, to which these values respond differently, must determine the values of K_2 and of $1/K_1$. Indeed we must assume that the ranges of molecular movement and orientation mechanisms differ for

TABLE II
ARRANGEMENT OF THE ELASTOMERS ACCORDING TO
INCREASING VALUES OF Δa_1 AND Δa_2 .

No.	Ranked according to Δa_1	No.	Ranked according to Δa_2	
1.	Vulkollan	-8.8	1. Vulkollan	-245
2.	Natural rubber A 1	-8.7	2. Buna S III A 17 (Heat Softened)	-48
3.	Natural rubber A 11	-5.8	3. Neoprene RT	-35
4.	Coral rubber	-5.2	4. Oppanol B 200	-29
5.	Natural rubber A-34 (Defo 250)	-4.0	5. Natural rubber A-34	-26
6.	Oppanol B 200	-2.4	6. Perbunan	-24
7.	Neoprene RT	-2.1	7. Polymar SX 371	-24
8.	Polymar SX 371	-0.3	8. Natural rubber A 11	-18
9.	Buna S III, A 17 (Heat Softened)	-0.1	9. Coral rubber	-16
10.	Perbunan	+2.2	10. Buna S III, raw, A-16	-10
11.	Buna S III, raw, A 16	+2.5	11. Natural rubber A 1	-6
12.	Polybutadiene	+5.2	12. Cold rubber, SBR 1500	+4
13.	Cold rubber, SBR 1500	+5.6	13. Polybutadiene	+27

From this we can conclude that the common fundamental molecular processes which determine the sign of the deviations, are superimposed on specific processes, which affect $1/K_1$ and K_2 to different extents or in a completely opposite way, processes which determine the numerical values of these "constants."

mechanical deformation and for stress-optical measurements. Kuhn and Gr \ddot{u} n² divide the force which is effective in producing an elongation into an orienting and a stretching component, so that the orienting fraction serves merely to steer the segments into preferred directions, while the stretching component is used so that "the filamentary molecules are not only oriented by the pulling, but are also stretched, and partly uncoiled." (Kuhn calculates the ratio of these force fractions: stretching: orienting = 5:3.)

The value of the double refraction at a given orientation is determined by the so-called anisotropy of the polarizability of the "favorable" filamentary molecules. This quantity, which is derived from the constants K_1 or $1/K_1$ accordingly stays, under fixed circumstances, in close relationship with the constitution of the chain molecule. We can therefore derive important expressions from it about molecular properties.

Of course, these relationships are extraordinarily complex, and up to the present are not to be considered as adequately clear qualitatively and even less so in a quantitative sense; we therefore confine ourselves to looking up and formulating this relation in a general way. The anisotropy of the polarizability of a filamentary molecule depends on two factors:

1. The intensity of the interatomic fields of force within the molecular chain.
2. Their spatial distribution and interactions (linkages). In general, the more strongly "directional" a molecular chain, the more pronounced its anisotropy.

Chain molecules with a great variety of atoms, atomic groupings, and types of bonds are found in the various elastomers. The bonds within the individual macromolecules are without doubt stable in the temperature range here considered of 10° to 90° C. The primary anisotropy contribution which is due to the macromolecules should then be considered as independent of temperature. The temperature dependence of $1/K_1$ is then given by Equation (11a), according to Kuhn and Gr \ddot{u} n \ddot{u} s.

$$\left[\frac{1}{K_1} \right]_T = \frac{n}{(n^2 + 2)^2} \cdot \frac{45k''T}{2\pi(\alpha_1 - \alpha_2)} = \frac{n}{(n^2 + 2)^2} \cdot a'T \quad (11A)$$

The temperature coefficient a_1 of $1/K_1$ is accordingly

$$a_1 = \frac{n}{(n^2 + 2)^2} \cdot \frac{45k''}{2\pi(\alpha_1 - \alpha_2)} \quad (11B)$$

The term $n/(n^2 + 2)^2$ was brought into the constant a_1 in order to improve the comparison of the respective temperature coefficients. The effect of the temperature dependence of this term is not very great in the range of the tests.

However, we may imagine that anisotropy in "real" elastomers is not determined by the primary bonds, but that secondary bonds of all sorts between and within the chain molecules influence the anisotropy factor. These secondary valence bonds—as has been explained in the discussion of the temperature function of the modulus of elasticity—should not be thought of as being thermally stable. The temperature dependence of the value of $1/K_1$, as found in experiments with various elastomers, shows that the "anisotropy-tensor" changes with temperature. We can think of these changes as being traced back to a loosening of the secondary valences by heat, so that the anisotropy of the polarizability is changed. This however means that a particular temperature coefficient of the stress-optical constant, K_1 or $1/K_1$, can show a positive or negative deviation from the theoretical value. The temperature dependence of the reciprocal of the stress-optical constant, $1/K_1$, is discussed in the following because of its better comparability with the elastic modulus (it has the same dimension as the E modulus). The consequences in regard to K_1 are apparent.

It is difficult to foretell the way in which the intermolecular bond mechanisms will affect the anisotropy factor. Any such predictions would have a speculative character in the present state of our knowledge. Conversely, it is just as difficult to draw any definite conclusions about the nature of the secondary bonds based on the change of anisotropy with temperature. It is possible, however, that the large amount of research data which is given, can serve theoretical physics as a basis and starting point for the more exact formulation of theories on the connections between secondary bonds and anisotropy.

We wish to point out that for the most part the elastomer systems which we have studied show a negative deviation, Δa_1 , of the temperature coefficient of $1/K_1$ from the theoretical value. From that we must conclude that the optical anisotropy of these elastomers increases with rising temperature. If we check the deviations, Δa_2 , of the temperature coefficients of the E modulus in these

systems, we find that they too with but few exceptions show negative tendencies (See Table II). It is seen that $1/K_1$ and K_2 are dimensionally similar; each may be considered as a modulus, that is to say, a force which is used to produce a certain effect. In one case it is the force used to reach a certain elongation, in the other it is the force used to attain a definite double refraction. Both of the constants also indicate that the force is used to bring about a certain orientation, although the "favorable" ranges of orientation are different. With similar indications from Δa_2 and from Δa_1 we can well suppose that the "elementary processes" which cause the deviations likewise are similar. Yet it is also found that ranking the elastomers on the one hand according to the values of Δa_1 and on the other according to the values of Δa_2 shows no agreement in their sequence. This is shown in Table II (silicone rubber is omitted).

We should expect that the comparison of the temperature functions of $1/K_1$ and of K_2 would make possible a better differentiation of the characteristics of the elastomers than the onesided consideration of the temperature coefficient of only one of these quantities. This will be further clarified. To the extent that the indications from Δa_1 and Δa_2 for the chosen elastomer are in agreement, we should certainly assume that the molecular-physical interpretation given by us for Δa_2 should also hold essentially for the deviation of the temperature coefficient of $1/K_1$ from the theoretical value. This interpretation is here outlined again in order to give a better comprehension of the relationships:

1. Negative deviations. Loosening of sites of secondary valence adhesion, so called "secondary crosslinks". In this case the overall degree of crosslinking diminishes with rising temperature, and the elastic modulus is consequently reduced. In the case of the reciprocal of the stress-optical constant, the anisotropy term becomes larger with the dissolution of the sites and in this way the temperature coefficient is reduced. The destruction of secondary valence crosslinking points can also be accompanied by an increase of the modulus. This depends upon the fact that the number of the filamentary molecules is increased by the freeing of molecular chains which had previously held together in a "crystalline" way. In general, however, it is supposed that the modulus-depressing effect dominates.

2. Positive deviations. Dissolution of sites of blocking, which are the result of bulky molecular structure. So long as a portion of a molecule is hindered in its mobility, its contribution to the modulus will be lacking. This is true for the "modulus of elongation", K_2 , as well as for the "double refraction modulus", $1/K_1$. Thus, with warming, the force grows stronger than expected and causes positive deviations in Δa_2 as well as in Δa_1 .

When we consider merely the sign of the deviations of Δa_1 and of Δa_2 we obtain greater certainty in the interpretation of the molecular processes, but we do not get any additional insight in regard to special elastomer properties. This chance is given when we review the rankings of the elastomers according to the values of Δa_1 and Δa_2 .

RELATIONSHIPS BETWEEN STRUCTURE AND THE MECHANICAL AND STRESS-OPTICAL BEHAVIOR

Most of the elastomer systems studied were vulcanized products; Oppanol alone is an uncrosslinked high polymer with elastomeric properties. A comparison of the temperature functions of the stress-optical constant and of the elastic modulus, in an attempt to draw conclusions about the picture of the elastomer properties, could be exact only if systems were used which were com-

parable in their degree of crosslinking and in their pretreatment. That would mean that the effect of the degree of crosslinking would have to be carefully investigated for each vulcanizable type of elastomer, and that the dependence of each one on prehandling (storage, milling, etc.) would have to be thoroughly studied. Such a program would have enlarged the range of this experimental work to unmanageable size. We have therefore contented ourselves by bringing the elastomers in question to a fairly comparable state of crosslinking by using amounts of compounding ingredients which were indicated by experi-

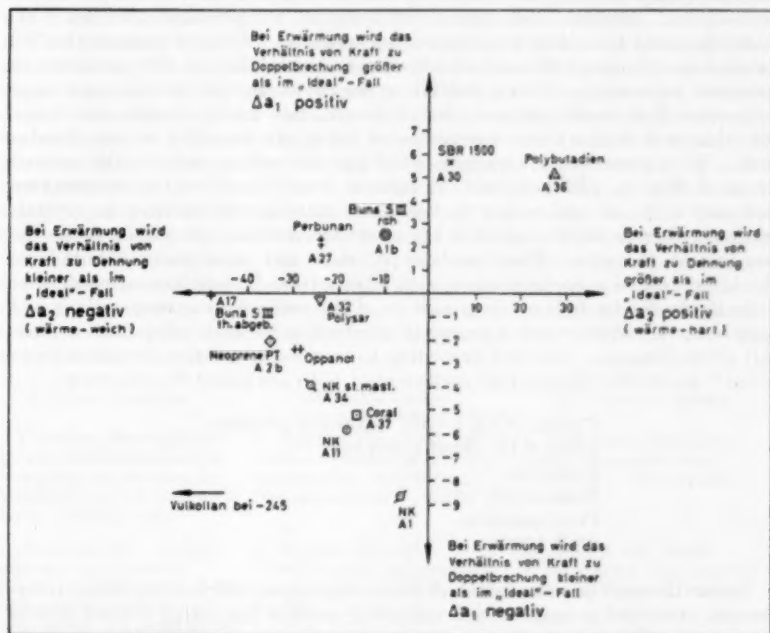


FIG. 4.—Deviations of various elastomers from thermal ideal behavior. Ordinate: Difference of the temperature coefficient of $1/K_1$ from the ideal value. Abscissa: Difference of the temperature coefficient of K_1 from the ideal value. Axis Intersection: "Ideal" rubber. On the Figure: (Top) With heating, the ratio of force to double refraction becomes greater than the "ideal" case. Δa_1 positive. (Left) With heating, the ratio of force to elongation becomes less than in the "ideal" case. Δa_2 negative. (Heat-softened). (Right) With heating, the ratio of force to elongation becomes greater than in the "ideal" case. Δa_2 positive. (Heat-hardened). (Bottom) With heating, the ratio of force to double refraction becomes less than in the "ideal" case. Δa_1 negative. On the points: NK = Natural rubber; th. abg. = heat softened; St. mast = heavily milled.

ence, and by standardizing the vulcanizing conditions. The effects of prehandling and vulcanization on the stress-optical constants, the elastic moduli and kindred temperature functions were apparent only in the case of natural rubber. Further mention of this will be made later.

In the first place we should now resume the line of thinking given at the end of the last section, and attempt to detect relationships between deviations of the temperature coefficients and molecular-physical properties, by comparative analyses of the relative positions of Δa_1 and Δa_2 for each elastomer.

A coordinate system is given in Figure 5 on whose ordinate are shown the

variations of the temperature coefficient of $1/K_1$ from the ideal values, and on whose abscissa are given the deviations of the temperature coefficient of K_2 from the ideal values. Each elastomer is represented by a point whose coordinates give a measure of its deviation from ideal mechanical deformation and stress-optical values. It can be seen that there is a certain grouping of the elastomer systems. The question now arises: to what extent do these locations agree with the known chemical and physical properties of the materials? Such an agreement can naturally be expected only for those material-specific properties which affect, on the one hand, the elastic modulus, and on the other, the stress-optical constant, and their dependence on temperature. We have already discussed these factors in preceding sections. We may suppose that all material-specific properties which affect the orientability of the molecules or molecular segments in either a positive or negative sense will have a much more noticeable effect on the orientation-double refraction and its temperature function, than will temperature dependence of the elastic modulus or the modulus itself. If we consider the arrangement of the elastomer systems in the vertical direction, that is, with respect to deviations from "ideal" of the temperature coefficient $1/K_1$, we will notice that all those materials which show no crystallization, either in the stretched or the unstretched states, are found above the zero line on the plot. These are the polymers and copolymers of butadiene which, because of numerous side chains arising from 1,2-addition or because of steric hindrance by bulky side groups or of the confused occurrence of *cis* and *trans* isomers, cannot reach a degree of orientation which is adequate for (partial) crystallization. Ranked according to increasing positive deviation from "ideal", Δa_1 of the temperature coefficient of $1/K_1$ are found the following:

Polysar SX371 (just below the abscissa).
Buna S III (heat softened).
Perbunan.
Buna S III, crude.
Polybutadiene.
SBR 1500.

Below the zero line are found all those elastomers which show X-ray interferences, stretched or unstretched, indicating more or less highly defined fibrous structures. These are the high polymers which have particularly high strength, even without the addition of active fillers. It is very interesting that the arrangement of these systems according to the increasing negative deviation from "ideal" of the temperature coefficient, $1/K_1$, gives the same sequence that is indicated by their crystallizability. From this we may, of course, note that there is no quantitative measure of crystallization tendency, but that we have only phenomenological knowledge of it:

Neoprene RT—No clear information is to be found about its chemical composition and crystallizing tendency. It is probably a copolymer. Most Neoprenes, however, because of their high contents of *trans* isomer, show no such clearly evident tendency to crystallize as does natural rubber.

Oppanol B 200—(polyisobutylene). Because of its symmetrical structure—both methyl groups attached to a single carbon atom—it can crystallize at normal temperatures at elongations of 500 to 700%.

Natural rubber—(natural polyisoprene). Can partially crystallize when kept at 15° C for sufficiently long periods of time. Distinct X-ray interferences are apparent with elongation above about 200%.

Coral rubber—(synthetic polyisoprene). The producers of this material found that it gave the same X-ray interferences with elongation as did natural rubber.

Vulkollan—(crosslinked isocyanate/polyester). Can show crystallization phenomena at room temperature and low elongations.

In discussing the grouping of the elastomer systems along the horizontal direction, the direction of the abscissa, we must recall the reflections made in the section "Interpretation of the Experimental Results. Temperature Dependence of the Elastic Modulus". The deviations, Δa_2 , from "ideal" values of the elastic modulus K_2 are plotted in this horizontal direction.

The interpretation of the arrangement of the high polymers in terms of their position along the abscissa is unfortunately not possible by means of such a simple and unique viewpoint as is used in the differentiation according to their position along the ordinate (deviations of $1/K_1$ from the theoretical temperature coefficients). The thermolabile "secondary network", which is responsible for the deviations Δa_2 , can be the result of secondary valence forces or of steric hindrance by side groups. Which of these two factors is the one which most strongly controls the temperature behavior of the elastic modulus can be determined only by the position relative to the abscissa. The latter divides the materials into two groups, the sterically hindered uncrystallizable elastomers above the abscissa and the crystallizable symmetrical elastomers, with or without polar groups, under the abscissa. This may be examined more closely when the individual elastomer systems are considered with respect to the ranking of their abscissas:

I. Under the abscissa	II. On the abscissa Δa_2 Negative	III. Above the abscissa
1. Vulkollan. Strongly polar; symmetrical structure. Secondary crosslinking by secondary valence forces; readily crystallizable. 2. Neoprene RT. Polar; relatively symmetrical structure. Secondary crosslinking by secondary valence forces. Crystallizable. 3. Natural and Coral Rubbers. Nonpolar; symmetrical structure. Weak secondary valence forces. Crystallizable.	1. Buna S III. (heat softened). Weakly polar; unsymmetrical structure. Not crystallizable. 2. Polysar SX 372. Weakly polar; unsymmetrical structure. Not crystallizable.	1. Perbunan. Strongly polar; unsymmetrical structure. Not crystallizable. 2. Buna S III, crude. Weakly polar; unsymmetrical. Not crystallizable. 3. SBR 1400. Weakly polar; Very unsymmetrical. Not crystallizable. 4. Polybutadiene. (Polymer with high conversion). Weakly polar; extremely branched and unsymmetrical. Not crystallizable.

Δa_2 positive.

As can be seen, a fairly good diagnosis of the structural nature of an elastomer can be made by a study of the material's position on such a $\Delta a_1/\Delta a_2$ coordinate system as given above; indeed there is the possibility of obtaining a quantitative numerical measure of the polarity—something that has not been

previously possible—if we make use of Δa_1 and Δa_2 in the characterization. An objective differentiation of this characteristic which is important to technological applications of elastomers has accordingly become possible with a certain amount of experimental expense.

EFFECT OF VULCANIZATION ON THE MECHANICAL STRESS-OPTICAL BEHAVIOR OF NATURAL RUBBER

In this case of the "ideal" rubber, the elastic modulus is dependent upon the degree of vulcanization, but the stress-optical constant is not. We have studied natural rubber in several recipes and at several states of cure. The vulcanization reagents only were varied in the different recipes. Fillers were not included in the compounds, and this was true for all the other vulcanizates studied here. In this way, we showed that the stress-optical constant, and of course, its reciprocal, is affected by the vulcanization; that is in contrast with an "ideal" rubber. In order to fill out the picture, we have extended our research to tests on unvulcanized natural rubber, but we confined ourselves to experiments at room temperature.

As would be expected, we cannot define the behavior for the unvulcanized state by means of Equations (1) and (10). The quantities K_2 and $1/K_1$ for unvulcanized natural rubber just do not have the characteristics of constants. That is readily understandable in the case of the elastic modulus K_2 , for the material is quite plastic and will tend to adjust to stresses by fluid behavior. The measured values are dependent on the time of flow and as a result are well defined only when the period of time for the experiment is taken into consideration, as is done in Table III. The dependence of K_2 and $1/K_1$ (or K_1) on the time of the experiment is of course only apparent in case of real high polymers and of crosslinked systems, when the experimental time is commensurable with the relaxation time of the bonding mechanism. For the crosslinked systems which were studied, the experiment time is much greater than the relaxation time of the elastomeric binding mechanisms, so that the dependence practically fails to affect the results of the measurements. On the other hand, the macro-Brownian flow movements in unvulcanized rubber are so slow that they become quite evident in the experimental times fixed by the test conditions.

As is seen in Table III, $1/K_1$ also is not constant with time. Its values vary rather progressively with elongation and with time. In order to get comparable values, all the measurements were referred to the specific period of 100 seconds (by graphic interpolation). If we now compare the measurements for the unvulcanized and the vulcanized systems, it is seen in Table III that there is no correlation between the quantities K_2 and $1/K_1$. That also is to be expected. When we further examine the variation in the values of $1/K_1$ to find their connection with other experimental factors which bring about these variations, we notice that the $1/K_1$ value for natural rubber is highest for latex film (dried latex). This value decreases:

1. With elongation of the material (unvulcanized).
2. With milling of the material.
This decrease caused by the milling process is seen directly on the one hand and on the other is carried over to the vulcanizate.
3. With vulcanization, that is:
 - a) Longer curing time.
 - b) Higher curing temperature.
 - c) Higher sulfur content.

A decrease in the value of $1/K_1$ is interpreted as meaning that the mobile molecular segment becomes more strongly anisotropic. According to the statements in the preceding section, by way of comparison, a decrease in $1/K_1$ (based on the theoretical value) is more pronounced in the more easily crystallizable elastomers. It was intimated that we should understand the responsible molecular process as follows: Molecules which are bound by secondary valences to a neighboring molecule over a considerable length and thus have tendencies toward crystalline orientation are loosened from each other. This process was caused by rising temperature in the investigation cited. From this we can expect the value of the anisotropy to rise so that the value of $1/K_1$ decreases. We must assume—if the hypothesis is valid—that it is concerned with a region of submicroscopic dimensions, the preliminary stages of crystalline orientation.

It is indeed natural to try this explanation for the decreases in $1/K_1$ values which are under discussion here but it must be kept in mind that the changes are brought about by other factors, that is, those enumerated previously. If we assume the general applicability of these ideas, then this would mean that

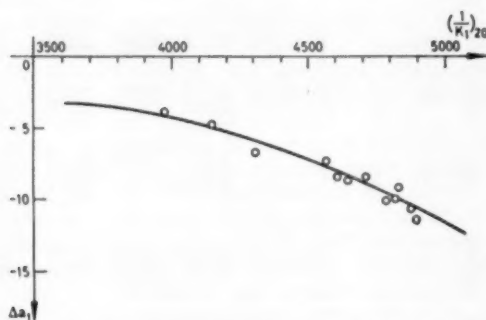


FIG. 5.—Relationship between the values of Δa_1 and $(1/k_1)_\infty$.

all of the factors listed help to loosen the couplings of the natural rubber molecule, which in the original latex state is relatively strongly "laterally" associated. This means that the smaller the $1/K_1$ value the more closely natural rubber approaches the "ideal" state. This conception is supported by the experimental results which show that there is a direct correlation between the Δa_1 and $1/K_1$ values. This is apparent in Figure 5. There it is shown that falling values of $1/K_1$ are associated with falling negative values of Δa_1 .

We can, to be sure, also suppose that it is not only the weakening of secondary valence bonds which is responsible for the reduction of $1/K_1$ values, but that other specific chemical reactions of the sulfur and/or of the accelerators with the rubber molecule have a part in it. In the case of the degradation of unvulcanized rubber by milling, oxygen also plays a part as a "bonding partner" with the natural rubber molecule. Such explanations are not to be arbitrarily rejected even though, in our opinion, they are not very close to the uncomplicated character of the experimental results.

Earlier work by Thibodeau and McPherson⁴ shows a pronounced increase in the stress-optical constant (and thus a decrease in $1/K_1$) with an increased degree of vulcanization. Treloar⁵ explains this behavior by ring-formation along the chain which becomes more and more effective with increase in the

amount of sulfur. The statements by Alphen¹⁰ about the cyclizing and crosslinking actions of sulfur during vulcanization may also be considered in this connection. These ideas originate in an entirely different context, but they can possibly serve to stimulate the interpretation of the results of our research. The same is true for the interesting and comprehensive chemical and reaction-kinetics studies on vulcanization by Scheele and his coworkers¹¹ as well as the further work of other authors.

Moreover, reference should be made to the work of Holt and McPherson¹², who found that the tendency for crystallization of natural rubber upon stretching decreased with increasing sulfur content.

The changes which the elastic modulus and its temperature coefficient undergo due to the various factors are more difficult to explain. During vulcanization, crosslinking and degrading reactions run concurrently. The elastic modulus which first increases with the crosslinking reaction, falls off as soon as the degradative reaction (so called "reversion") surpasses the crosslinking. (According to Flory¹³:

$$G = g S R T \left(1 - \frac{2M_c}{M} \right)$$

where G = elastic modulus, S = density, R = universal gas constant, T = absolute temperature, g = an individual material constant, M_c = molecular weight of the chain segment between two crosslink points, M = molecular weight of the rubber molecule. The modulus decreases with any decrease of M due to degradation). This phenomenon is shown fairly well by the data in Table III. There the tests made at various vulcanization times are grouped as follows:

Tests with increasing time at 125° C; A4, A5, A6

Tests with increasing time at 143° C; A3, A1, A2

Tests with increasing sulfur, vulcanized for the same time; A9, A1, A10

Reversion can be noted in the two series A4, A5, A6 and A3, A1, A2.

It is more difficult to explain the course of the respective Δa_2 values. In the case of the series A4, A5, A6, the values of Δa_2 run through a minimum. At present, we have no explanation for this. In the case of the series A3, A1, A2 as well as in the one for increasing sulfur, A9, A1, A10, the Δa_2 value goes through a maximum. Perhaps this maximum may be explained if we think of the advancing vulcanization as progressively hindering the plastic deformation of the test specimen (macro Brownian movement) and the system thus approaches closer to the "ideal" rubber (from the Δa_2 point of view). The macro-Brownian movement mechanism is practically halted at the point of optimum vulcanization, while the micro-Brownian movement of the chain segments between sites of crosslinking is free. The entropy-elasticity here passes through a maximum while the energy-elasticity shows a minimum. Beyond the point of optimum vulcanization, the energetic portion of the elastic modulus is most probably on the increase with the advancing vulcanization. According to van Alphen¹⁰ sulfur forms not only heat stable bridges between the rubber molecules, but also forms cyclic bonds of other kinds and it is to be expected that they affect the modulus, but not by way of the entropy mechanism. It may also be pointed out that hard rubber is decidedly "heat-softenable". The rubber molecule also becomes more strongly polar with increasing sulfur combination, and further reduction of the Δa_2 value because of this seems reasonable. We have shown graphically in Figure 6, the rather complex effect

of the sulfur dosage, which is indicated in the values in Table III. The maximum in the values of Δa_2 is quite clearly shown there.

In an article by Treloar¹⁴, tests are described in which a natural rubber vulcanizate was cooled in the stretched state after it had been allowed to relax in the extended state at higher temperature. A practically "ideal" modulus/temperature function was found during the cooling. We have also performed these tests, but the elongation was limited to about 100 per cent, whereas

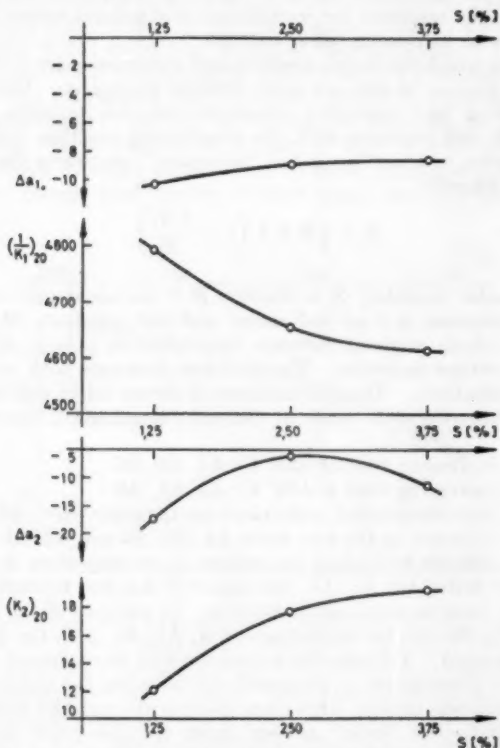


FIG. 6.—Effect of increasing sulfur content on different characteristics of natural rubber vulcanizates.

higher elongations were described in the above mentioned work. Moreover, we changed the procedure in our work, so that the measurements were also made during the warming. The pieces were prestretched twenty times at room temperature, as we have previously described. We likewise measured the elongation-double refraction as we did in all our other tests. The research data are given in Table IV. In the "repetitions" which are introduced for the vulcanizates already presented in Table III, we are dealing with compounds which were prepared about a year after the originals. The data indicated by I and II were measurements made on test samples which were stamped from the same vulcanized sheet.

TABLE IV
MECHANICAL AND STRESS-OPTICAL MEASUREMENTS ON NATURAL RUBBER
VULCANIZATES WITH COOLING AND RELAXATION

See Table III for recipes and vulcanization data. See text for descriptions of the tests. The values calculated for "ideal" rubber are based only on the "warming" and "cooling" processes.

Identification	° C	Operation	K_2 Measured		$\frac{1}{K_1}$ Measured	
			$\frac{Kg}{cm^2}$		$\frac{Kg}{cm^2}$	
A 7 Repetition I	26.7	Warming	18.6	18.6	4950	4950
	50.8	↓	19.0	↓	5210	↓
	89.3	↓	19.8	22.5	5440	6100
	89.5	Relaxation after 3 hrs	18.9	18.9	5440	5440
	28.2	Cooling (stretched)	18.0	15.7	4860	4440
	27.8	Relaxation after 20 more hrs.	17.7	—	4860	—
A 7 Repetition II	25.0	Warming	18.5	18.5	4910	4910
	50.2	↓	19.0	↓	5160	↓
	87.6	↓	19.8	22.4	5430	6110
	87.8	Relaxation after 3 hrs.	19.6	19.6	5350	5350
	30.0	Cooling (stretched)	18.5	16.5	5000	4430
	26.2	Relaxation after 20 more hrs.	18.2	—	4910	—
A 9 Repetition I	25.0	Warming	12.1	12.1	4760	4760
	50.1	↓	13.2	↓	5050	↓
	85.0	↓	14.5	14.5	5320	5800
	85.0	Relaxation after 3 hrs	13.6	13.6	5110	5110
	29.6	Cooling (stretched)	11.9	11.5	4670	4350
	27.8	Relaxation after 20 more hrs.	11.5	—	4760	—
A 9 Repetition II	24.3	Warming	12.8	12.8	4920	4920
	50.9	↓	13.6	↓	5130	↓
	86.4	↓	14.2	15.5	5300	6060
	86.5	Relaxation after 3 hrs.	14.2	14.2	5400	5400
	28.6	Cooling (stretched)	12.8	12.0	4830	4470
	26.3	Relaxation after 20 more hrs.	12.6	—	4790	—

The results are single determinations, except the data under "warming", and therefore are not as accurate as the data given in Tables I and II. Nevertheless, it can be clearly seen that the values for "cooling" follow a curve which runs somewhat parallel to the one for "warming". These curves are somewhat displaced from each other because of the changes following the "relaxation."

From these experiments, we take it to be possible to get a nearly "ideal" cooling relationship between the elastic modulus and temperature in the case of a suitably chosen vulcanizate. We can confirm the statements made by Treloar on this point. To be sure, we do not believe that we should decide from this finding that this vulcanizate corresponds to the "ideal" rubber, because the cooling curve of $1/K_1$ measured with the same test specimen is in no way "ideal".

From the ideas that have been given we would say that the trend of the values of $1/K_1$ as shown in Table IV make it plain that the secondary valence of bonds which are loosened by warming, are, for the greater part, established again by cooling. It should of course be noted that the time necessary for the cooling amounted to three or four hours.

SUMMARY

The temperature functions of the elastic modulus K_2 and of the stress-optical constant K_1 or its reciprocal $1/K_1$ were investigated for several elastomers. In the case of a hypothetical rubber which we have called "ideal" rubber—in analogy to gases—theory requires a direct proportionality between K_2 or $1/K_1$ and the absolute temperature. The temperature functions of K_2 and $1/K_1$ which we found by experiments with "real" elastomers show characteristic negative and positive deviations Δa_2 and Δa_1 from "ideal" values. When we put these values of Δa_2 and Δa_1 into a coordinate system, we find a certain orderly arrangement of the different elastomers, which allows us to picture a relationship between molecular structure and the values of Δa_2 and Δa_1 . This brings up the possibility of explaining the experiments with the help of already known molecular-physical concepts. Although other explanations are conceivable the attempt is made to develop the simplest and most obvious ideas.

It is conjectured that negative values of Δa_2 and Δa_1 come about from a loosening of secondary valence bonds—in certain ways, like crystal bonds—between neighboring molecules. Negative Δa_1 values were found only in the crystallizable elastomers.

It is further conjectured that positive values of Δa_2 and Δa_1 may result from the liberation by heat, of blocked, bulky molecular segments. These molecular segments can then contribute to the entropy elasticity only at higher temperatures. Positive Δa_2 and Δa_1 values are found chiefly in strongly crosslinked elastomers.

Brief attention is given to the physical processes which are responsible for the elongation—double refraction and the entropy-elasticity. From this, it seems that the stress-optical constant and its temperature function are connected with properties of the molecular chains and on their orientability and crystallizability. The elastic modulus and its temperature function are strongly affected by the structure of the network and the molecular cohesive forces. Worthwhile hints about crystallization tendency, polarity and degree

of symmetry of the different systems are given by the Δa_1 and Δa_2 values in the above mentioned coordinate systems.

Natural rubber was tested in different recipes. The results of milling, of sulfur and accelerator additions, of time and temperature of vulcanization, on the values of K_2 , $1/K_1$, Δa_2 and Δa_1 were all investigated. The values of $1/K_1$ are at their highest level for dried latex films (unvulcanized). Milling and vulcanization, particularly the use of rather long periods and high temperatures, lower the value of $1/K_1$. A drop in the value of $1/K_1$, which regularly appears with a reduction of the negative Δa_1 value, is explained as a loosening of secondary valence molecular couplings. According to this, natural rubber in the latex state is most strongly associated. According to this explanation, stretching in the unvulcanized condition is sufficient to loosen the secondary valence molecular bonds. Milling and vulcanization also act to loosen the linkages. Secondary valence bonds which are loosened by warming, as a general rule, are reestablished by prolonged cooling. It is to be supposed that the secondary valence molecular bonds under consideration are limited to small regions, somewhat comparable to the ordering in liquids.

With an increasing degree of vulcanization, the Δa_2 values go through a maximum which perhaps coincides with the condition of optimum vulcanization. This is explained as a maximum of the entropy-elasticity. In the case of slightly milled natural rubber which is appropriately vulcanized, the value of Δa_2 can become practically zero. The change of the elastic modulus with temperature then is "ideal." Nevertheless, no "ideal" rubber exists here, for Δa_1 is less than zero.

REFERENCES

- ¹ Müller, F. H., *Kolloid-Z.*, **95**, 138 (1941).
- ² Kuhn, W. and Gr \ddot{u} n, F., *Kolloid-Z.*, **101**, 248 (1942).
- ³ Meyer, K. H., and Ferri, C., *Helv. Chim. Acta*, **18**, 570 (1935).
- ⁴ Kuhn, W., *Kolloid-Z.*, **76**, 258 (1936).
- ⁵ Meyer, K. H., Susich, G. V. and Valko, E., *Kolloid-Z.*, **59**, 208 (1932).
- ⁶ Kuhn, W., *Kolloid-Z.*, **68**, 2 (1934); *Kolloid-Z.*, **76**, 258 (1936).
- ⁷ Guth, E. and Mark, H. F., *Monatsh. Chem.*, **65**, 93 (1934).
- ⁸ See also Pohl, "Lehrbuch der Physik, Bd 3. Optik u. Atomphysik", Springer-Verlag, Berlin, 1954.
- ⁹ Footnote 5 in H. A. Stuart, "Die Physik der Hochpolymeren, Bd. III. Ordnungszustände und Umwandlungserscheinungen in festen hochpolymeren Stoffen", Springer-Verlag, Berlin, 1955, p. 324.
- ¹⁰ Alphen, J. V., *Angew. Chem.*, **66**, 7 (1957).
- ¹¹ Scheele, W. and coworkers. Current publications in *Kautschuk u. Gummi*.
- ¹² Holt, W. L. and McPherson, A. T., *J. Research Nat. Bur. Standards*, **17**, 657 (1936).
- ¹³ Flory, P. J., *Chem. Revs.*, **35**, 51 (1955).
- ¹⁴ Treloar, L. R. G. in H. A. Stuart, "Die Physik der Hochpolymeren", Bd. IV. "Theorie und Molekulare Deutung Technologischer Eigenschaften von Hochpolymeren Werkstoffen", Springer-Verlag Berlin, 1956, p. 295.

EFFECT OF REDOX SYSTEMS ON THERMAL OXIDATIVE PLASTICIZING OF BUTADIENE-ACRYLONITRILE RUBBER *

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The method of mechanical plasticization at present used for butadiene-acrylonitrile rubbers has very low output and the main method of softening styrene-butadiene rubber—thermal oxidative plasticization—cannot be used for nitrile rubbers, because it causes them to stiffen. Therefore, work has recently been conducted on accelerating the thermal plasticization of nitrile rubbers. It was found that if a redox system consisting of iron salts plus dimethylphenyl-*p*-cresol (DMPPC) is introduced into the latex, butadiene-acrylonitrile rubbers capable of thermal plasticization can be obtained¹.

In the present article a study of the structural changes in nitrile rubbers which result from thermal oxidative plasticization in the presence of a redox system are presented and the molecular structure of the softened rubbers is related to the properties of vulcanizates.

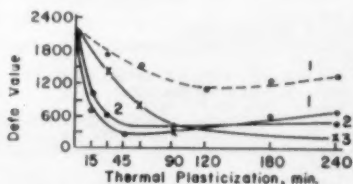


Fig. 1.—Variation in the Defo value with temperature and time of thermal plasticization, for normal-production (---) and experimental (—) butadiene-acrylonitrile (82:18) rubbers: 1—140° C; 2—130° C; 3—120° C.

Butadiene-acrylonitrile rubbers with three monomer ratios were used: 82:18, 74:26 and 60:40. The redox system was introduced into normal-production latex of these rubbers. The optimum amount of DMPPC was two parts by weight for the (82:18) copolymer and three parts by weight for the other two copolymers. Thermal plasticization was conducted in a pan with a circulation of air. The air pressure used for the (82:18) and (74:26) copolymers was 3 atmospheres, and for the (60:40) copolymer, 4 atmospheres. The structural changes which occurred were followed by the viscoelastic properties of the softened rubbers as well as by solution properties.

Figures 1–6 show the changes in the Defo value (stiffness) and elasticity of experimental and normal-production nitrile rubbers depending on the plasticization time and temperature. The results show that when experimental (82:18) and (74:26) copolymers containing DMPPC were subjected to thermal

* Translated by M. Lambert from *Kauchuk i Rezina*, No. 11, pages 17–20 (1959); a RABRM translation; see *Soviet Rubber Technology*, No. 11, 1959.

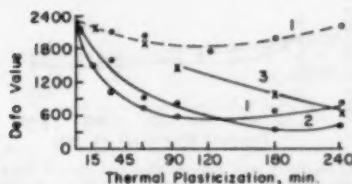


FIG. 2.—Variation in the Defo values with temperature and time of thermal plasticization, for normal-production (---) and experimental (—) butadiene-acrylonitrile (74:26) rubbers: 1—140° C; 2—130° C; 3—120° C.

oxidative plasticization, as in the case of similar normal-production rubbers, processes of breakdown and structure formation (branching or crosslinking) occur simultaneously, though at very different rates in the two cases.

In normal production nitrile rubbers the rate of breakdown is slight and structure formation predominates, whereas with the experimental rubbers there was a considerable increase in the rate of breakdown, structure formation being

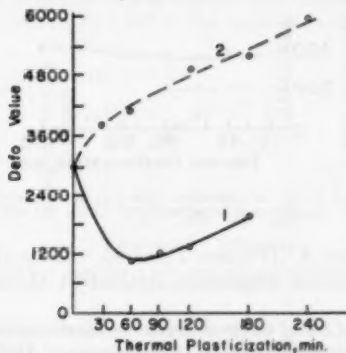


FIG. 3.—Variation in the Defo value with time of thermal plasticization at 140° C, for experimental butadiene-acrylonitrile (60:40) rubbers: 1—experimental rubber; 2—normal-production rubber.

largely suppressed. When the experimental (82:18) and (74:26) rubbers were subjected to thermal oxidative plasticization under the conditions used for normal-production rubber, a soft rubber of any plasticity could be obtained (Defo value 1000 *g* and lower). When the redox system was introduced into butadiene-acrylonitrile (60:40) rubber, although the rate of breakdown increased, a rubber with a Defo value of less than 1000 *g* could not be obtained.

As can be seen from the results, the behavior of the experimental rubbers during thermal oxidative plasticization is determined mainly by acrylonitrile

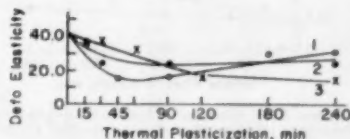


FIG. 4.—Variation in the Defo elasticity with temperature and time of thermal plasticization, for experimental butadiene-acrylonitrile (82:18) rubber: 1—140° C; 2—130° C; 3—120° C.

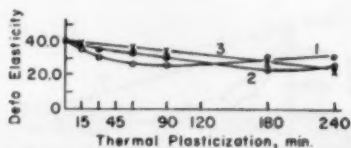


FIG. 5.—Variation in the Defo elasticity with temperature and time of thermal plasticization, for experimental butadiene-acrylonitrile (74:26) rubber: 1—140° C; 2—130° C; 3—120° C.

content. As this increases, the rate of breakdown decreases while that of structure formation increases. Butadiene-acrylonitrile (82:18) rubber has the highest rate of breakdown, and a (60:40) copolymer the lowest.

That structure formation increases as the content of nitrile groups increases is also confirmed by the fact that with the experimental (60:40) rubber, in contrast to the other two experimental copolymers, solubility decreases even in the initial stages of treatment, and crosslinked insoluble structures are formed. With (82:18) and (74:26) rubbers branched but soluble structures form at the beginning of thermal plasticization, indicated by the steady increase in the

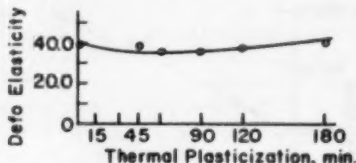


FIG. 6.—Variation in the Defo elasticity with time of thermal plasticization at 140° C, for experimental butadiene-acrylonitrile (60:40) rubber.

hydrodynamic coefficient K' (Figures 7 and 8). It should be noted that this coefficient can give only a qualitative evaluation of the relative degree of branching.

Effect of the temperature of thermal oxidative plasticization on the properties of softened butadiene-acrylonitrile rubbers.—The curves of Defo value and elasticity for the experimental (82:18) and (74:26) rubbers (see Figures 1, 2, 4, 5), as well as those of the coefficient K' for their solutions (see Figures 7 and 9), show that as the temperature of thermal oxidative plasticization is raised the rate of breakdown increases, though at the same time structure-formation increases. Because of this, softened rubbers obtained at a higher temperature have a higher Defo elasticity, while their solutions have a lower intrinsic viscosity and a higher value of K' , than thermally softened rubbers with the same Defo value but obtained at a lower temperature (Table 1).

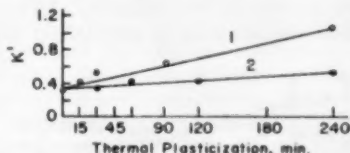


FIG. 7.—Variation in the coefficient K' of solutions of butadiene-acrylonitrile (82:18) rubber with time and temperature of thermal plasticization: 1—130° C; 2—120° C.

* Exactly what is meant by the "hydrodynamic coefficient" is not known though it is obviously a measure of the extent to which the flow of the solution departs from pure viscous flow. (Translator.)

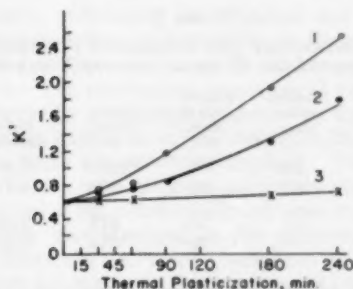


Fig. 8.—Variation in the coefficient K' of solutions of butadiene-acrylonitrile (74:26) rubber with time and temperature of thermal plasticization: 1—140° C; 2—130° C; 3—120° C.

The optimum temperature for thermal oxidative plasticization of the experimental (82:18) and (74:26) rubbers was 130° C, as at this temperature a sufficiently high rate of breakdown is achieved in the initial stages of the process. As the temperature is raised to 140° C the rate of breakdown increases, but

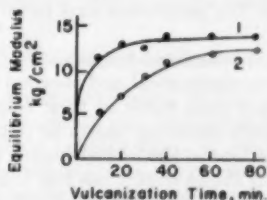


Fig. 9.—Variation in the equilibrium modulus of pure gum vulcanisates of butadiene-acrylonitrile (82:18) rubber with vulcanization time: 1—thermally softened rubber; 2—mechanically softened rubber.

structure-formation also increases. On the other hand, when the temperature is lowered to 120° C the rate of structure-formation decreases considerably, though the rate of breakdown becomes too low.

For the experimental (60:40) rubber the optimum temperature was 140° C as only at this temperature is the degree of breakdown appreciable. At 120° and 130° C the Defo value does not generally decrease.

TABLE I

EFFECT OF PROCESSING CONDITIONS ON THE PLASTO-ELASTIC PROPERTIES OF THERMALLY PLASTICIZED NITRILE RUBBERS, AND OF THEIR SOLUTIONS

Rubber	Plasticization temp., °C	Plasticization time, min	Defo value g	Defo elasticity	Intrinsic viscosity $[\eta]$	K'
Butadiene-acrylonitrile (82:18) copolymer	140	90	325	1.72	0.70	1.85
	120	120	300	1.58	1.48	0.42
	130	90	425	2.37	1.11	0.60
	130	240	450	2.43	1.07	0.96
Butadiene-acrylonitrile (74:26) copolymer	140	30	1025	3.00	1.00	0.77
	120	180	1000	2.80	1.06	0.70
	140	60	713	2.60	0.86	0.83
	140	180	700	2.93	0.78	1.93
	120	240	700	2.25	0.98	0.76

TABLE 2
PROPERTIES OF MECHANICALLY AND THERMALLY PLASTICIZED BUTADIENE-
ACRYLONITRILE (74:26) RUBBERS AND OF THEIR SOLUTIONS

Rubber	Plastici- sation temp., ° C	Plastici- sation time, min	Defo value, g	Defo elasticity	Intrinsic viscosity [η]	K'
Thermally plasticized	120	180	1000	2.80	1.06	0.70
	130	180	375	2.21	0.76	0.31
Mechanically plasticized	—	30	975	2.05	1.17	0.25
	—	20	375	0.48	0.99	0.24

Comparison of the properties of softened butadiene-acrylonitrile rubbers obtained by mechanical and thermal oxidative plasticization.—To evaluate more accurately the differences in the properties of softened rubbers obtained by mechanical and thermal oxidative plasticization, rubbers with the same Defo value (i.e., having approximately the same degree of breakdown) were compared. An accurate quantitative evaluation cannot be made in this way (the softened rubbers were not fractionated, and differences in their properties may be caused also by different molecular weight distributions in the "cold" and "hot" soft rubbers), though the properties can nevertheless be qualitatively compared.

The properties of softened butadiene-acrylonitrile (74:26) rubbers with the same Defo value, obtained by mechanical and thermal oxidative plasticization, are shown in Table 2 together with those of their solutions. A mechanically softened rubber has lower Defo elasticity than one obtained by thermal oxidative plasticization, while solutions of the former have a higher intrinsic viscosity and lower values of K' . This shows that it has less branching than a thermally softened rubber. The properties of solutions of (60:40) rubbers softened by mechanical and thermal oxidative plasticization cannot be compared, as during the initial stages of thermal plasticization an insoluble gel is formed.

Structural differences between the softened rubbers are confirmed by the equilibrium moduli of pure gum vulcanizates made from mechanically and thermally softened butadiene-acrylonitrile (82:18) rubbers with the same Defo value (Figure 9). The modulus was determined by the method described in the literature². With a similar amount of combined sulfur (1.75–1.80%) vulcanizates based on a thermally softened rubber have higher equilibrium moduli (approximately 14 kg/cm²) than those of a mechanically softened rubber (ap-

TABLE 3
EFFECT OF THE METHOD OF PLASTICIZATION ON THE MECHANICAL PROPERTIES OF
VULCANIZATES OF STANDARD NITRILE RUBBER STOCKS

Rubber	Plasticization	Defo value, g	Vulcani- zation time, min	Tensile strength, kg/cm ²	Breaking elongation, %	Tension set, %	Rebound resilience, %
Butadiene- acrylonitrile (74:26) copolymer	Thermal	1000	40–60	273–282	630–656	19–23	28–29
	Mechanical	975	40–60	292–310	630–730	17–20	30–31
Butadiene- acrylonitrile (60:40) copolymer	Thermal	1050	50	273	550	30	13
	Mechanical	1100	50	333	610	30	11

proximately 11 kg/cm²). Obviously the branched and crosslinked structures formed during thermal oxidative plasticization are the cause of this.

Effect of the method of plasticization on the mechanical properties of vulcanizates of nitrile rubbers.—The mechanical properties of vulcanizates of standard stocks made from thermally plasticized experimental and mechanically plasticized normal-production butadiene-acrylonitrile (74:26) and (60:40) rubbers with the same Defo value are shown in Table 3. The vulcanizates of the thermally softened rubbers have slightly lower strength, breaking elongation and elasticity than those of the mechanically softened rubbers.

A similar difference was observed in the properties of vulcanizates of mechanically and thermally softened butadiene-styrene rubbers^{3,4}. The authors explained these differences by the formation of branched and crosslinked structures in the thermally softened rubber, as well as by the accumulation of a low-molecular fraction. Obviously the same occurs for butadiene-acrylonitrile rubbers. This explanation is also confirmed by the fact that the greatest difference in the properties of the vulcanizates is observed in the (60:40) copolymer, where structure-formation develops to a larger extent. Despite the lower mechanical properties of vulcanizates of thermally softened butadiene-acrylonitrile rubbers compared with mechanically softened counterparts, those of the former are still sufficiently high to enable thermal oxidative plasticization to be applied industrially.

CONCLUSIONS

1. By using a redox system consisting of iron salts plus dimethylphenyl-paracresol, the rate of breakdown was considerably increased and structure-formation suppressed. This enables thermal oxidative plasticization to be used in industry for butadiene-acrylonitrile rubbers.

2. As the number of nitrile groups in the polymer increases, the rate of breakdown during thermal oxidative plasticization decreases and structure-formation occurs more rapidly. Butadiene-acrylonitrile (82:18) rubber has the greatest rate of breakdown, and the (60:40) copolymer the highest rate of structure-formation.

3. Vulcanizates of stocks based on thermally softened experimental butadiene-acrylonitrile rubbers are slightly inferior as regards strength and elasticity to similar vulcanizates of mechanically softened rubber. Their properties are, however, sufficiently high to enable thermal oxidative plasticization to be applied industrially.

LITERATURE

- ¹ Novikov, A. S. and Devirts, E. Ya., *Vestnik Khim. prom.*, No. 7, 1958.
- ² Vishnitskaya, L. A., "Works of the Scientific Research Institute of the Rubber Industry," No. 1, 1954, p. 53.
- ³ Beta, G. E. and Karmin, B. K., "Studies in the Physics and Chemistry of Rubber," published by Goskhimizdat, 1950, p. 94.
- ⁴ Novikov, A. S., et al., "Works of the Scientific Research Institute of the Rubber Industry," No. 1, 1954, p. 3.

MODIFICATION OF CARBON BLACK WITH IONIZING RADIATIONS *

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It is well-known that the reinforcing properties of carbon blacks used as active fillers for rubber depend to a considerable extent upon the adsorption properties of the surface of the carbon black particles. The presence on this surface of atoms and groups of polar or apolar character chemically bound with it, the surface relief and the presence of atoms with unsatisfied valencies in the hydrocarbon framework of the elementary crystallites determine the specific adsorption properties of carbon black of various types.

In the present investigation we demonstrate the possibility of modifying the surface of the carbon blacks by the action of ionizing irradiation and by the radiochemical "sewing-up" of various compounds on their surface. Such modified carbon blacks have a considerable influence upon the physico-chemical properties of the resulting vulcanizates, which may make it possible to create new materials.

The investigation was devoted to: (1) Ukhta thermal black—a typical representative of the soft semireinforcing blacks (practically not oxidized); (2) channel black from the same works—a hard active black, having a markedly oxidized surface, capable of irreversible interaction with the surface of the rubber and with the compounding ingredients.

The irradiation of the carbon blacks was carried out on a Co⁶⁰ source of activity 22,000 gram equivalents. The carbon blacks were subjected to the action of the radiation in sealed ampoules in a vacuum and in air. For a series of experiments the carbon blacks were evacuated at a vacuum of 10^{-4} to 10^{-5} mm mercury column for a prolonged period at 280 to 300°. The preparation of the carbon blacks for the investigation of the "sewing-up" of the various chemical substances on their surface took the following form: on the carbon blacks, previously washed with benzene and dried, there were adsorbed physically in separate series of experiments PBNA (phenyl-2-naphthylamine), MBT, (mercaptobenzothiazole), sulfur and SKS-30A styrene-butadiene rubber, after which the excess of these substances were removed and the blacks dried. After irradiation the blacks were added to the rubber on the mill, 60 parts by weight to 100 of rubber. From the stock thermovulcanizates were prepared; for this purpose sheets were pressmolded for 30 min at 60° and then vulcanized for 30, 40 or 60 min in an electric press at 220°.

The mechanical properties of the vulcanizates were investigated on a Polyani (?Translator) dynamometer. We determined the equilibrium modulus (E_{∞}) and the dependence of the true stress (σ) upon elongation.

Thermal black.—Irradiation of a thermal black whether in air or in vacuum makes it softer. This effect is greater with irradiation in vacuum. The data are given in Table I.

On increasing the radiation dosage the hardness of the black increases.

* Translated by R. J. Moseley from *Khim. Nauka i Prom.* 4, No. 3, 407-8, 1959; a RABRM translation.

TABLE I
ALTERATION IN THE EQUILIBRIUM MODULUS OF THERMOVULCANIZATES OF
SKS-30A PREPARED WITH PREVIOUSLY IRRADIATED THERMAL BLACKS

Treatment of black	Dosage, r	Equilibrium modulus, kg/sq cm
None	0	9.8
Irradiated in air	46.10 ⁶	6.0
Irradiated in vacuum	46.10 ⁶	4.7

However even with large dosages (243·10⁶r) thermovulcanizates produced with such black have lower moduli than thermovulcanizates with nonirradiated black.

The irradiation of carbon black with substances previously physically adsorbed on its surface (MBT, PBNA, sulfur and SKS-30A rubber) leads to a marked alteration in the properties, reflected in the mechanical properties of vulcanizates based on SKS-30A with these blacks. Such alterations are evidently effected by the radiochemical "sewing-up" of a portion of the adsorbed substance, i.e., by chemical bonding of it to the surface of the blacks. In Table II we present data characterizing thermovulcanizates based on SKS-30A with modified carbon blacks added to them.

TABLE II
ALTERATION IN THE EQUILIBRIUM MODULUS OF THERMOVULCANIZATES BASED ON
SKS-30A PREPARED FROM CARBON BLACKS WITH COMPOUNDING
INGREDIENTS "SEWN" INTO THEM (RADIOCHEMICALLY)

Thermal black and chemical "sewn" on	Dosage, r	Equilibrium modulus, kg/sq cm
Black irradiated in air	46.10 ⁶	6.0
SKS-30A rubber	52.10 ⁶	6.7
PBNA	52.10 ⁶	7.9
MBT	52.10 ⁶	9.0
Sulfur	52.10 ⁶	11.1

Channel black.—Irradiation of channel black (dosage 50·10⁶r) in air has little influence upon its reinforcing properties. Irradiation in vacuum makes it very much less hard ($E\infty$ increases from 22.5 to 29.4 kg/sq cm, and the static modulus increases analogously).

On the surface of the channel black, as in the previous case, there were adsorbed SKS-30A rubber, MBT, PBNA and sulfur, whereupon the carbon black was subjected to irradiation (dosage 50·10⁶ r). The addition of such blacks to thermovulcanizates showed that their properties alter with no set rule, contrary to thermal black, the modification of whose surface leads to an increase in the modulus (Table 2). The most considerable effect is produced on irradiation of a channel black with chemically adsorbed rubber. Thus the equilibrium modulus for thermovulcanizates with this carbon black is equal to 37.5 kg/sq cm, while $E\infty$ for a vulcanizates with a carbon black irradiated in the absence of rubber is 24.4 kg/sq cm.

A THEORY OF THE THERMODYNAMIC BEHAVIOR OF NONELECTROLYTE SOLUTIONS. II. APPLICATION TO THE SYSTEM RUBBER-BENZENE *

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INTRODUCTION

The theories of polymer solutions proposed by Flory¹, Huggins,² Miller³, and Guggenheim⁴ employ the concept of a coiling polymer molecule which may become entangled with other such molecules in solution, and utilize statistical-mechanical considerations to obtain the thermodynamic relations attending the solution or mixing process. The theories of Flory and Huggins are essentially identical, as are those of Miller and Guggenheim. Further, all theories reduce to practically the same result when the molecular weight of the polymer is high.

The present status of these theories may be summarized as follows. Except for dilute solutions, the free energies of mixing predicted by theory agree generally quite well with those measured experimentally; however, the heats and entropies of mixing do not. To correct the situation in the dilute region, Flory and Krigbaum^{5,6} developed a special theory which preserves the original model used by Flory, but attempts to take into account the lesser tangling of polymer chains as the solution is diluted. The latter theory appears to work quite well in very dilute solutions, but it suffers from two shortcomings. First, the theory does not apply to concentrations high enough to overlap the original theories, and hence there is a concentration gap for which no theory is available. Second, the Flory-Krigbaum theory employs parameters which are different in significance from those used at the higher concentrations, and, thus far, no relation has been established between them. The result is that polymer solution behavior at low concentrations is expressed in terms of one set of parameters, that at higher concentrations in another, and no means are available to connect these or to cover the concentration gap to which neither theory applies.

Recently Maron⁷ developed a theory of the thermodynamic behavior of nonelectrolyte solutions which is nonstatistical in character, and which expresses the behavior of solutions in terms of parameters whose significance remains unaltered over the full concentration range of the solution. The purpose of the present paper is to show the application of this theory to the system rubber-benzene, for which Gee and Treloar⁸ have determined at 25° C the free energies, heats, and entropies of mixing over the entire range of concentration from pure benzene to pure rubber. Subsequent papers in the series will give applications of the theory to osmotic pressure and light scattering behavior of polymer solutions, as well as to the thermodynamic behavior of solutions of low molecular weight substances.

* Reprinted from the *Journal of Polymer Science*, Vol. 40, pages 59-71, 1959.

THE FREE ENERGY OF MIXING FOR RUBBER-BENZENE SOLUTIONS

In the discussion which follows the subscript 1 will invariably refer to the solvent, here benzene, and the subscript 2 to the solute, rubber.

If we consider the solution of N_2 moles of rubber in N_1 moles of benzene to form one mole of solution, then according to Maron's theory⁷ the integral free energy of mixing, ΔF_m , is given by

$$\Delta F_m = N_1 \overline{\Delta F}_1 + N_2 \overline{\Delta F}_2 \quad (1a)$$

$$= RT(X^\circ + \mu N_1 v_2) \quad (1b)$$

where $\overline{\Delta F}_1$ and $\overline{\Delta F}_2$ are partial molal free energies, and X° is

$$X^\circ = \ln(V^\circ/V) + N_1 \ln v_1 + N_2 \ln v_2 + N_2 \ln(\epsilon/\epsilon^\circ) \quad (2)$$

In these equations N_1 and N_2 are the mole fractions of the constituents in solution, v_1 and v_2 are the volume fractions, μ is an interaction parameter, V° is the total volume of the constituents before mixing, and V is their volume after mixing. Again, the quantity ϵ is the effective volume factor^{7,9} of the polymer in solution at any volume fraction v_2 , and ϵ° is the effective volume factor for the noncrystalline polymer in bulk. From Equation (1b) the partial molal free energies of the two constituents follow as:

$$\overline{\Delta F}_1 = RT[X_1 + (\mu - \sigma v_1)v_2^2] \quad (3)$$

$$\overline{\Delta F}_2 = RT[X_2 + (\mu + \sigma v_2)xv_1^2] \quad (4)$$

where

$$X_1 = \ln(V^\circ/V) + \left(\frac{V^\circ_1}{N_1 V^\circ_1 + N_2 V^\circ_2} - \frac{\bar{V}_1}{N_1 \bar{V}_1 + N_2 \bar{V}_2} \right) + \ln v_1 + [1 - (\epsilon/\epsilon_0 x)]v_2 \quad (5)$$

and

$$X_2 = \ln(V^\circ/V) + \left(\frac{V^\circ_2}{N_1 V^\circ_1 + N_2 V^\circ_2} - \frac{\bar{V}_2}{N_1 \bar{V}_1 + N_2 \bar{V}_2} \right) + \ln v_2 + (\epsilon/\epsilon_0 - x)v_1 + \ln \epsilon/\epsilon^\circ \quad (6)$$

In the latter equations, V°_1 and V°_2 are the molar volumes of the two pure constituents, \bar{V}_1 and \bar{V}_2 are their partial molal volumes in solution, $x = V^\circ_2/V^\circ_1$, ϵ_0 is the effective volume factor for the polymer at $v_2 = 0$, and $\sigma = (\partial\mu/\partial v_2)_T$.

Since the volume changes attending the solution of rubber in benzene are small, we shall assume them to be zero. Then $V^\circ = V$, $V^\circ_1 = \bar{V}_1$, $V^\circ_2 = \bar{V}_2$, and Equations (2), (5), and (6) reduce to

$$X^\circ = N_1 \ln v_1 + N_2 \ln v_2 + N_2 \ln(\epsilon/\epsilon^\circ) \quad (7)$$

$$X_1 = \ln v_1 + [1 - (\epsilon/\epsilon_0 x)]v_2 \quad (8)$$

$$X_2 = \ln v_2 + [(\epsilon/\epsilon_0) - x]v_1 + \ln(\epsilon/\epsilon^\circ) \quad (9)$$

Further, ϵ/ϵ_0 is given by^{7,9}

$$\epsilon/\epsilon_0 = 1/[1 + (\epsilon_0 - \epsilon_\infty)v_2] \quad (10)$$

where ϵ_∞ , the effective volume factor for the polymer at tightest packing in solution, may be taken as 4.0, while $\epsilon_0 = [\eta]_{v_2}/2$, $[\eta]_{v_2}$ being the intrinsic viscosity of the solution when the concentration is expressed in volume fractions.

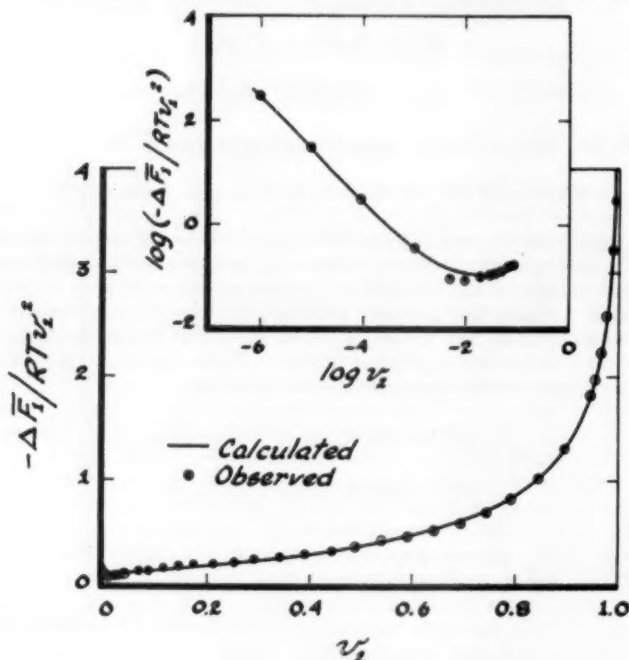


FIG. 1.—Plots of $-\overline{\Delta F}_1/RTv_2^2$ vs. v_2 for rubber in benzene at 25° C.

The use of the available information¹⁰ on intrinsic viscosities of rubber in benzene as a function of molecular weight M_2 yields for $[\eta]_{v_2}$,

$$[\eta]_{v_2} = 1.60 \times 10^{-3} \rho_2 M_2 \quad (11)$$

where ρ_2 is the density of the rubber. In their work Gee and Treloar⁸ found their sample of rubber to have a molecular weight of 280,000 grams/mole, and, taking $\rho_2 = 0.9116$ g/cc, we obtain $[\eta]_{v_2} = 408$, $\epsilon_0 = 204$, and $\epsilon_0 - \epsilon_\infty = 200$. Finally, since no information is available on the packing of rubber in bulk, we shall assume it to be 0.74, which yields $\epsilon^\circ = 1/0.74 = 1.35$.

For the application of Equations (8) and (9) we need also $x = V_2^\circ/V_1^\circ$. From the molecular weights and densities of the two solution constituents we obtain $x = 3430$.

Using now these values of the ϵ 's, we calculated X° for the various concentrations for which Gee and Treloar gave data at 25° C. Again, their values of

$\Delta\bar{F}_1$ and $\Delta\bar{F}_2$ were combined through Equation (1a) to give ΔF_m . From these values of X° and ΔF_m , the values of μ were then calculated through Equation (1b). Over the concentration range of $v_2 = 1 \times 10^{-6}$ to $v_2 = 0.994$, the values of μ were found to be constant within experimental error, and to equal $\mu = 0.400 \pm 0.011$. This constancy of μ at 25° C indicates that σ in Equations (3) and (4) is zero. Therefore, to check the μ calculation, the values of μ were also

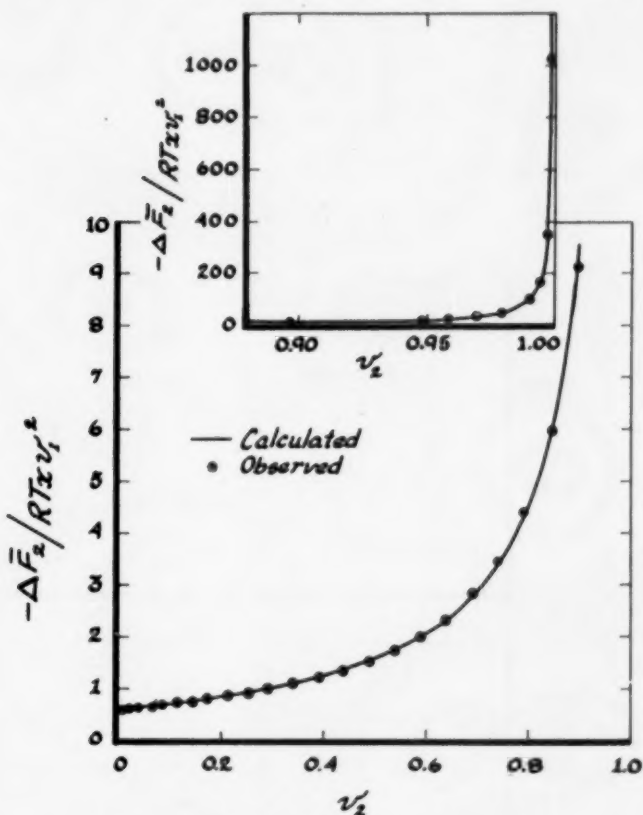


FIG. 2.—Plots of $-\Delta\bar{F}_2/RTxv_2^2$ vs. v_2 for rubber in benzene at 25° C.

evaluated from the $\Delta\bar{F}_1$ values of Gee and Treloar by use of Equations (3) and (8). The results again showed μ to be constant within experimental error and to equal $\mu = 0.394 \pm 0.021$. The agreement between these two sets of μ values is very satisfactory. Again, how well Equations (3) and (4) with $\mu = 0.394$ reproduce the experimentally observed values of $\Delta\bar{F}_1$ and $\Delta\bar{F}_2$ may be judged from Figures 1 and 2, where the solid lines give the calculated values, while the points represent experimental data. The insets in both figures give expanded plots of the data at the two ends of the concentration range.

THE HEAT OF MIXING

According to the new theory, the integral and partial heats of mixing are given by⁷

$$\Delta H_m = -T\lambda(RTN_1v_2) \quad (12)$$

$$Q_{H1} = \overline{\Delta H}_1/RTv_2^2 = -T\lambda + T\sigma'v_1 \quad (13)$$

$$Q_{H2} = \overline{\Delta H}_2/RTxv_1^2 = -T\lambda - T\sigma'v_2 \quad (14)$$

where

$$\lambda = (\partial\mu/\partial T)_{v_2} \quad (15)$$

and

$$\sigma' = (\partial\lambda/\partial v_2)_T = (\partial\sigma/\partial T)_{v_2} \quad (16)$$

On subtracting Equation (14) from Equation (13) we obtain

$$\begin{aligned} Q_{H1} - Q_{H2} &= T\sigma'(v_1 + v_2) \\ &= T\sigma' \end{aligned} \quad (17)$$

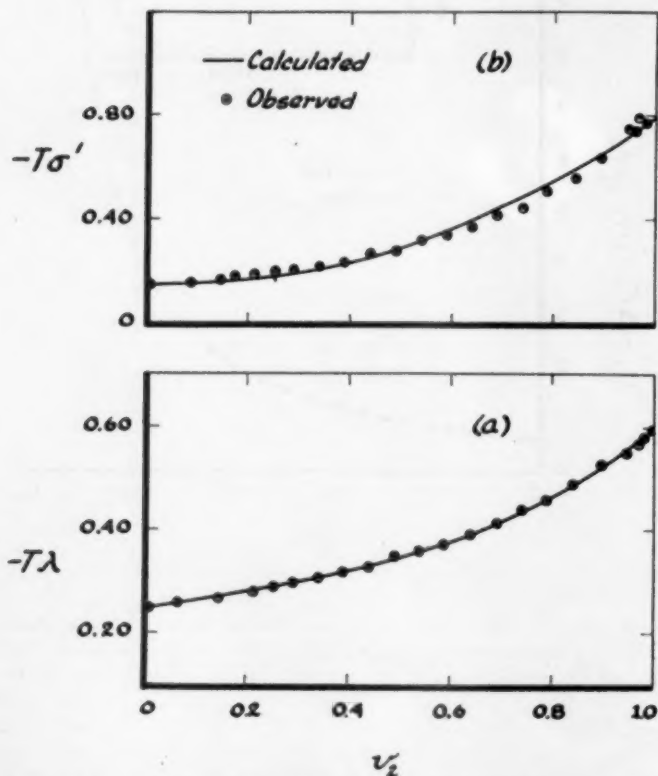


FIG. 3.—Plots of $-T\lambda$ and $-T\sigma'$ vs. v_2 for rubber in benzene at 25° C.

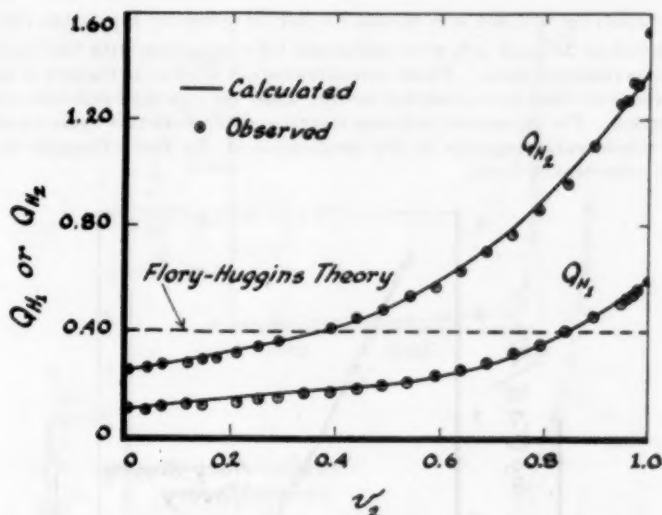


FIG. 4.—Plots of Q_{H1} and Q_{H2} vs. v_2 for rubber in benzene at 25° C.

and hence $T\sigma'$ may be found from the experimental values of $\overline{\Delta H_1}$ and $\overline{\Delta H_2}$. If $T\sigma'$ is known, $T\lambda$ follows then from either Equation (13) or Equation (14).

The values of $T\sigma'$ and $T\lambda$ obtained in this manner from the data of Gee and Treloar for rubber in benzene at 25° C are shown by the circles in Figure 3. The dependence of $-T\lambda$ on v_2 can be represented by the power series

$$-(T\lambda)_{25^\circ\text{C.}} = 0.25 + 0.15v_2 - 0.04v_2^2 + 0.24v_2^3 \quad (18)$$

and hence, in line with Equation (16), $-T\sigma'$ should be given by

$$-(T\sigma')_{25^\circ\text{C.}} = -T(\partial\lambda/\partial v_2)_T = 0.15 - 0.08v_2 + 0.72v_2^2 \quad (19)$$

Values of $T\lambda$ and $T\sigma'$ calculated by means of Equations (18) and (19) are given by the solid lines in Figure 3, and these agree quite well with the observed results.

Finally, Figure 4 shows a comparison of the observed values of Q_{H1} and Q_{H2} and those calculated by means of Equations (13) and (14) through use of Equations (18) and (19). The horizontal broken line in Figure 4 is the dependence of Q_{H1} and Q_{H2} on v_2 predicted by the Flory-Huggins theory.

THE ENTROPY OF MIXING

Maron's theory gives for the integral and partial entropies of mixing the expressions

$$\Delta S_m = -R[X^\circ + (\mu + T\lambda)N_1v_2] \quad (20)$$

$$\overline{\Delta S_1} = -R[X_1 + (\mu + T\lambda)v_2^2 - (\sigma + T\sigma')v_1v_2^2] \quad (21)$$

$$\overline{\Delta S_2} = -R[X_2 + (\mu + T\lambda)vv_1^2 + (\sigma + T\sigma')xv_2v_1^2] \quad (22)$$

On the basis of $\mu = 0.394$, $\sigma = 0$, and $T\lambda$ and $T\sigma'$ given by Equations (18) and (19), values of $\Delta\bar{S}_1$ and $\Delta\bar{S}_2$ were calculated for comparison with Gee and Treloar's experimental data. These comparisons are shown in Figures 5 and 6, where the solid lines are calculated results, while the experimental data are the open circles. The agreement between theory and experiment is again excellent, and is considerably superior to the predictions of the Flory-Huggins theory, given by the broken lines.

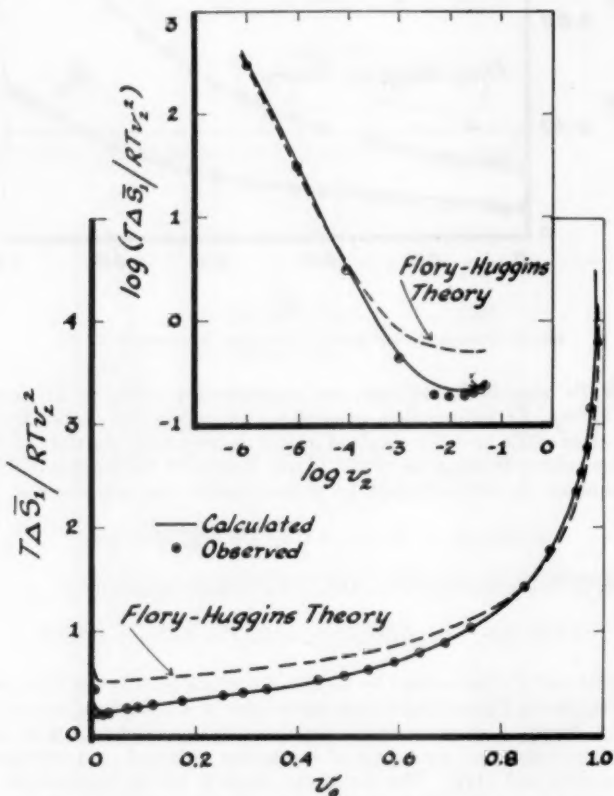


FIG. 5.—Plots of $T\Delta\bar{S}_1/RTv_2^2$ vs. v_2 for rubber in benzene at 25° C.

DEPENDENCE OF PARAMETERS ON TEMPERATURE

Although the heats of mixing of polymer solutions are strongly dependent on concentration, their variation with temperature is generally small over appreciable ranges of temperature. If it be assumed that the heat of mixing is independent of temperature, then it is readily possible to calculate the variation of μ , σ , $T\lambda$, and $T\sigma'$ with temperature and concentration, and thereby predict the thermodynamic behavior of rubber-benzene solutions at temperatures other than 25° C.

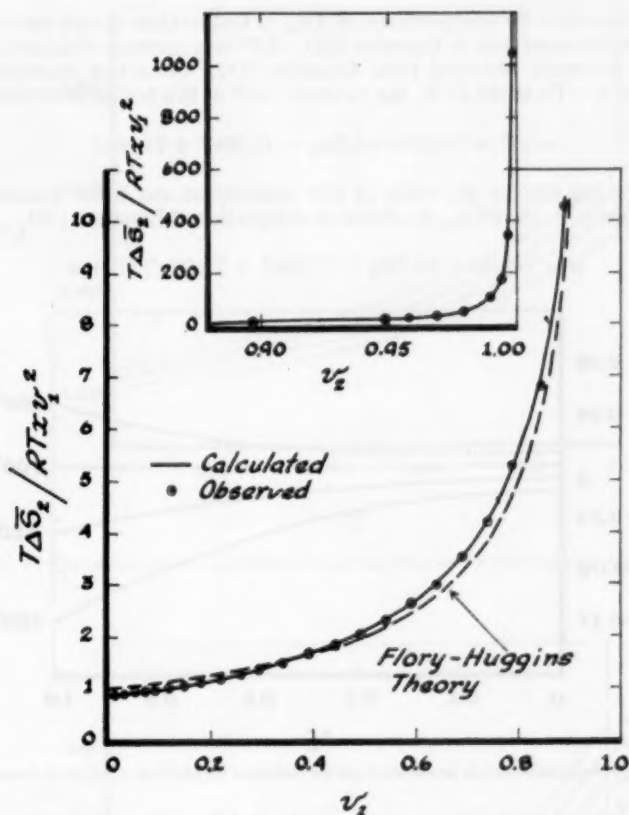


FIG. 6.—Plots of $T\Delta\bar{S}_2/RTxv_1^2$ vs. v_1 for rubber in benzene at 25°C.

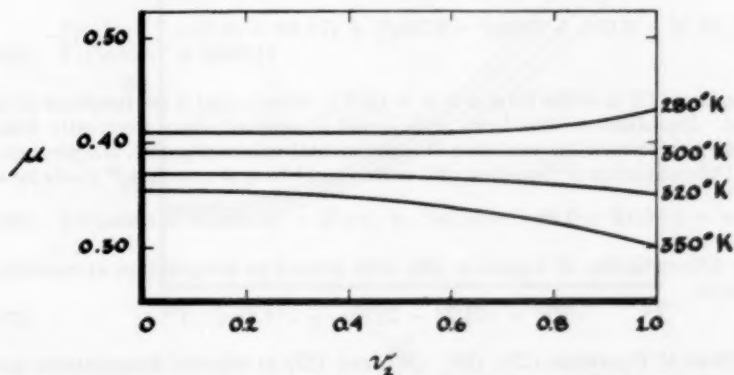


FIG. 7.—Dependence of μ on temperature and concentration for rubber-benzene solutions.

The condition for independence of ΔH_m of temperature is met very closely by the requirement that in Equation (12) $-\lambda T^2$ be a function of v_2 only. This function is readily obtained from Equation (18). Since this equation gives the value of $-\lambda T$ at 298.2° K, the value of $-\lambda T^2$ at this temperature follows as

$$-\lambda T^2 = 74.54 + 44.72v_2 - 11.93v_2^2 + 71.56v_2^3 \quad (23)$$

and this must also be the value of this quantity at any other temperature. Again, since $\lambda = (\partial\mu/\partial T)_{v_2}$, we obtain on integration of Equation (23)

$$\mu = (74.54 + 44.72v_2 - 11.93v_2^2 + 71.56v_2^3)/T + \alpha \quad (24)$$

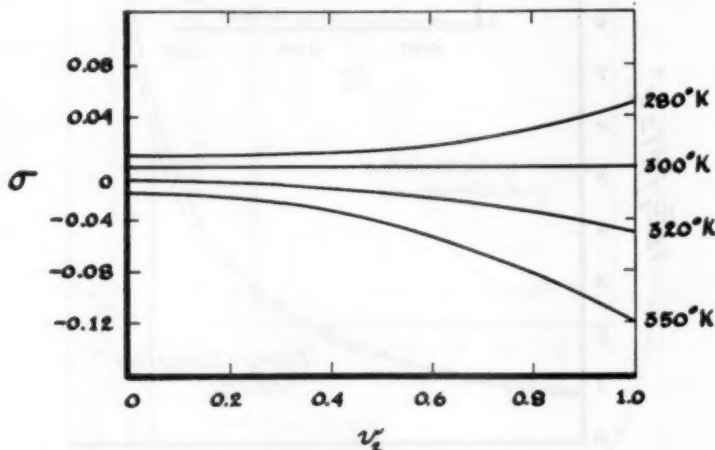


Fig. 8.—Dependence of σ on temperature and concentration for solutions of rubber in benzene.

The constant of integration, α , can be evaluated from the fact that $\mu = 0.934$ at 298.2° K. Thus, we obtain for μ as a function of v_2 and T the expression

$$\mu = (0.14 - 0.15v_2 + 0.04v_2^2 - 0.24v_2^3) + (74.54 + 44.72v_2 - 11.93v_2^2 + 71.56v_2^3)/T \quad (25)$$

Equation (25) is of the form $\mu = \alpha + (\beta/T)$, where α and β are functions of v_2 only. Equations of this form, with α and β constant, have frequently been found to represent the variation of experimental values of μ with temperature.

Differentiation of Equation (25) with respect to v_2 at constant T yields for σ

$$\sigma = (-0.15 + 0.08v_2 - 0.72v_2^2) + (44.72 - 23.86v_2 + 214.68v_2^2)/T \quad (26)$$

and differentiation of Equation (26) with respect to temperature at constant v_2 gives

$$-T\sigma' = (44.72 - 23.86v_2 + 214.68v_2^2)/T \quad (27)$$

Plots of Equations (23), (25), (26), and (27) at selected temperatures are given in Figures 7–10. Figure 7 shows that, for a given concentration, μ de-

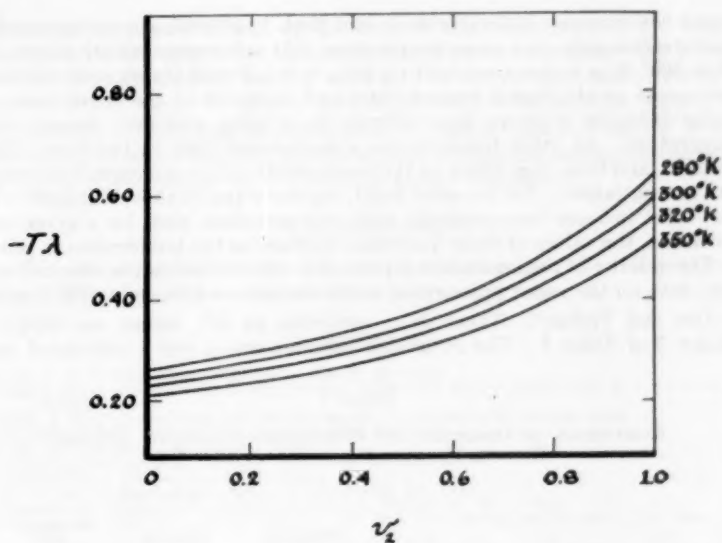


FIG. 9.—Dependence of $-T\lambda$ on temperature and concentration for rubber-benzene solutions.

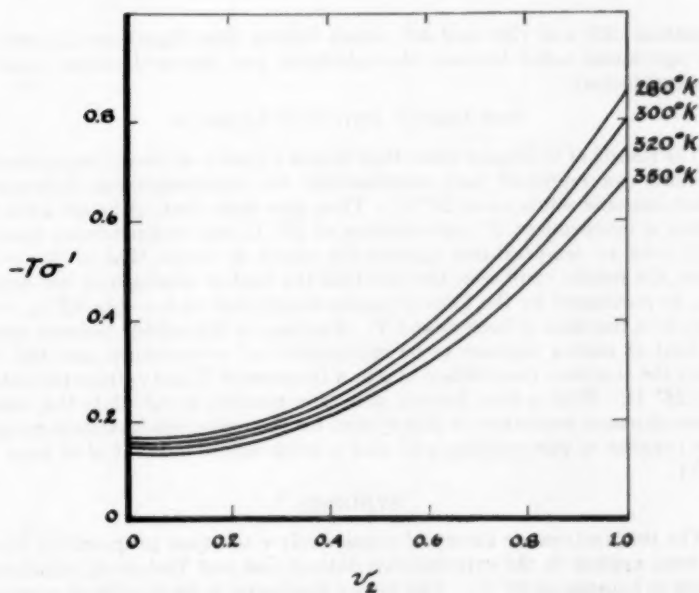


FIG. 10.— $-T\sigma'$ as a function of T and v_1 for rubber-benzene solutions.

creases with increase in temperature, and that, in general, μ is independent of concentration only near room temperature. At temperatures both above and below 300° K, μ is quite constant up to $v_2 = 0.5$, but at higher concentrations μ decreases at the higher temperatures and increases at the lower ones. A similar behavior is shown by σ (Figure 8), σ being zero only around room temperature. At other temperatures σ is constant only in the more dilute solutions, and then, depending on the temperature, either increases or decreases with concentration. On the other hand, Figures 9 and 10 show that both $-T\lambda$ and $-T\sigma'$ increase monotonically with concentration, and, for a given concentration, the values of these quantities decrease as the temperature is raised.

The validity of the arguments presented in this section can be checked with some data on the vapor pressures of rubber-benzene solutions at 100° C given by Gee and Treloar⁵. These data, converted to $\overline{\Delta F}_1$ values, are shown in column 5 of Table I. The remaining columns give μ and σ calculated from

TABLE I
COMPARISON OF OBSERVED AND CALCULATED VALUES OF $\overline{\Delta F}_1$ FOR
RUBBER-BENZENE SOLUTIONS AT 100° C

v_2	μ	σ	$\overline{\Delta F}_1$, calories/mole		
			Calculated	Observed	Deviation, %
0.579	0.316	-0.070	-126	-112	-3.8
0.771	0.299	-0.103	-379	-385	+1.6
0.913	0.282	-0.136	-950	-982	+3.3
0.944	0.278	-0.144	-1244	-1242	-0.2

Equations (25) and (26) and $\overline{\Delta F}_1$ which follows from Equations (3) and (8). The agreement noted between the calculated and observed values of ΔF_1 is very satisfactory.

DISCUSSION AND CONCLUSIONS

The results of this paper show that Maron's theory of binary nonelectrolyte solutions can represent very satisfactorily the thermodynamic behavior of rubber-benzene solutions at 25° C. They also show that, although μ for this system is independent of concentration at 25° C, this independence does not carry over to temperatures appreciably above or below that of the room. Again, the results emphasize the fact that the heat of mixing does not depend on μ , as postulated by the Flory-Huggins theory, but on $\lambda = (\partial\mu/\partial T)_{v_2}$, where λ can be a function of both v_2 and T . Further, in the rubber-benzene system the heat of mixing appears to be independent of temperature, and this fact allows the complete formulation of μ as a function of T and v_2 from the data at only 25° C. With μ thus known, it is then possible to calculate the various thermodynamic properties of this system for the entire concentration range of pure benzene to pure rubber, and over a temperature interval of at least 10-100° C.

SYNOPSIS

The thermodynamic theory of nonelectrolyte solutions proposed by Maron has been applied to the experimental data of Gee and Treloar on solutions of rubber in benzene at 25° C. The theory was found to be capable of representing these thermodynamic data very satisfactorily on the basis of a constant

interaction parameter μ , and on the basis of the dependence of the heat of mixing on the derivative of μ with respect to temperature rather than μ itself. Further, by assuming the heat of mixing to be temperature independent, an expression was set up for μ as a function of the volume fraction, v_2 , and the temperature. This equation reproduces $\overline{\Delta F_1}$ values measured at 100° C with an accuracy of better than 4%, and shows that at temperatures above and below 25° C μ is concentration- as well as temperature-dependent.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Flory, P. J., *J. Chem. Phys.* **9**, 660 (1941); *ibid.* **10**, 51 (1942).
- ² Huggins, M. L., *J. Chem. Phys.* **9**, 440 (1941); *J. Phys. Chem.* **46**, 151 (1942); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942).
- ³ Miller, A. R., *Proc. Cambridge Phil. Soc.* **39**, 54, 151 (1943); *Kolloid-Z.* **114**, 149 (1949).
- ⁴ Guggenheim, E. A., *Proc. Roy. Soc. (London)* **A183**, 203 (1944).
- ⁵ Flory, P. J., *J. Chem. Phys.* **17**, 1347 (1949).
- ⁶ Flory, P. J. and Krigbaum, W. R., *J. Chem. Phys.* **18**, 1086 (1950).
- ⁷ Maron, S. H., *J. Polymer Sci.* **38**, 329 (1959).
- ⁸ Gee, G. and Treloar, L. R. G., *Trans. Faraday Soc.* **38**, 147 (1942).
- ⁹ Maron, S. H., Nakajima, N. and Kreiger, I. M., *J. Polymer Sci.* **37**, 1 (1959).
- ¹⁰ Ewart, R. H., "Advances in Colloid Science", Vol. II, p. 238, Interscience Publishers, Inc., New York, 1946.

RECENT DEVELOPMENTS IN SUPERIOR PROCESSING NATURAL RUBBER

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In the few years since superior processing (SP) rubber was introduced to the rubber manufacturing industry its merits have steadily found wider acceptance.

A first publication described its composition and properties with particular reference to SP crepe¹, partly because the uses of SP rubber were expected to be mainly in products requiring lightness of color and purity of the raw rubber. Two British patents describe its use in the cable industry in continuous vulcanization and for high voltage cables².

SP smoked sheet equivalent to RSS-1 and SP air-dried sheet followed in late 1957 and SP brown crepe in early 1959. The production of SP rubbers in Malaya has been described³ and the British patent covering their production has recently been published⁴. The Rubber Research Institute of Malaya has given details of latest developments in SP rubber production⁵. These relate to forms of SP masterbatch, one of which is used in Malaya in the manufacture of SP brown crepe from estate and remillers' scrap. Development is proceeding to provide an SP masterbatch for use by the factory compounder to impart any desired degree of SP properties to any natural or general-purpose synthetic (SBR) rubber.

The present paper provides data of value to actual or potential users of these materials to supplement and amplify information already put forward⁶⁻⁸.

NATURE AND TYPES OF SP RUBBER

All SP rubbers contain a proportion (20%) of crosslinked rubber as microscopic particles intimately dispersed in a matrix of unvulcanized rubber. In SP sheet and SP first quality crepe the cross-linked units are the prevulcanized individual latex particles. In SP brown crepe they are produced by blending SP rubber in a concentrated form as a wet crumb with the appropriate grades of wet scrap rubber. A more recent development is the direct use by the factory compounder of SP rubber in a concentrated form; this is still in the evaluation stage, but enough is known about performance of the material to warrant a preliminary discussion. The particular concentrated SP rubber, which is in the form of a rough crepe intended for use as a component of the mix by addition to the base rubber of the compound, is known as SP90 crepe and is described by Sekhar and Drake⁵.

CONSEQUENCES OF TWO-PHASE STRUCTURE

The predominant characteristic of SP rubbers is their smoothness and shape stability at the intermediate stages of shaping the manufactured article prior to vulcanization. These stages may be carried out at higher viscosity levels than usual, so that compounds based on SP rubber are generally of higher

TABLE I
PROPERTIES OF SP RUBBERS

Two-phase structure 20/80 vulcanized/ unvulcanized rubber leads to	Properties in left-hand column result in
Higher raw Mooney viscosity. Higher viscosity stocks. Greater retention of viscosity on milling. Slightly reduced tack. Greater smoothness and shape—retention of masticated rubber. Faster vulcanizing characteristics.	Faster, smoother extrusions of lower die-swell over a wider temperature range. Firmer stocks for calender handling. Calendering at lower temperatures and higher viscosities. Adequate building tack. Hand building technique facilitated. Reduced sag and less distortion of extrusions. Greater regularity of calendered sheet dimensions. Reduced water marking in open steam cures. Less degradation of compounds on reworking. Easier preparation, reduced flow in storage, and improved physical properties of very soft compounds. Simplification of compound formulas with improved physical properties. Reduction in amount of vulcanizing ingredients for a given rate of cure.

apparent viscosity than their counterparts based on ordinary natural rubber of the same grade. To these two factors, the content of vulcanized rubber particles, conferring smoothness and shape stability, and the higher levels of compound Mooney viscosity, may be traced most of the characteristic properties of SP rubber. These, with their technological consequences, are summarized in Table I.

SP RUBBERS IN EXTRUSION

The main value of SP rubbers is in extrusion processes, where marked advantages are obtained with pure gum and moderately loaded compounds.

TABLE II
BEHAVIOR OF SP RUBBERS IN LABORATORY SOLID ROD EXTRUSIONS

Rubber	Pure gum compound					50 phr whitening compound				
	V ₁ ¹	Rpm ²	Rate extruded		Die swell, ⁴ %	V ₁ ¹	Rate extruded		Die swell, ⁴ %	
			Length, cm/min	Weight, g/min			Length, cm/min	Weight, g/min		
RSS (YO)	38	70	41	52	281	62	60	32	308	
SP RSS	40.5	70	64	56	120	64	112	38	161	
Air-dried sheet ³	46.5	20	12	15	229	58	57	31	318	
SP ADS	52	70	51	44	117	59	75	33	236	
Pale crepe	52.5	10	7	10	258	41	86	38	260	
SP crepe	48	70	50	54	131	43	123	38	160	

¹ Compound Mooney viscosity ML4, 212° F.

² Maximum rpm for smooth extrusion.

³ Sometimes known as pale amber unsmoked sheet (PAUS).

⁴ Die swell measured as volume increase of unit length of tubing of same section as die.

Pure gum compounds extruded through a 1/4-inch square die at 10-70 rpm. Whitening compounds extruded through 1/4-inch square die at 30 rpm. Extruder temperatures: pure gum, barrel 65° C, head 80° C, die 95° C. whitening, barrel 60° C, head 65° C, die 80° C.

The data given below, obtained with laboratory and larger equipment, illustrate the comparative behavior of SP with ordinary sheet and crepe in solid rod and tube extrusions.

In Table II are summarized the results obtained on extruding pure gum compounds through a $\frac{1}{4}$ -inch square die, and 20-volume calcium carbonate compounds through a $\frac{1}{4}$ -inch square die, from a 1-inch laboratory extruder. In pure gum compounds ordinary grades extruded smoothly only at lower speeds and then with much greater die swell than the corresponding SP grades. With a $\frac{1}{4}$ -inch round die the differences were even more striking. The compound based on ordinary RSS (Mooney viscosity 21.5) only extruded smoothly

TABLE III
EXTRUSIONS AT LOWEST EXTRUDABLE TEMPERATURE

Compound	Rubber	Mooney viscosity	Temp. of barrel, °C	Max. screw speed, rpm	Max. throughput		Die swell, %
					In/min	G/min	
Pure gum	RSS	72		Not extrudable			
	SP RSS	82		Not extrudable			
	RSS	52		Not extrudable			
	SP RSS	59	100	11	18	200	34
	RSS	39	90	11	13	200	49
	SP RSS	35	70	63	100	1000	25
50 Whiting	RSS	84	60	21	12	160	34
	SP RSS	94	60	40	64	610	20
	RSS	38	60	21	24	320	31
	SP RSS	54	60	63	102	940	20
125 Whiting	RSS	122	90	63	157	1704	24
	SP RSS	140	80	40	39	470	17
	SP RSS	140	90	63	161	1640	17
	RSS	40	60	11	32	420	20
	SP RSS	55	60	21	51	600	11
75 clay	RSS	58	70 ¹	63	50	430	10
	SP RSS	78	50	63	56	450	3
	SP RSS	78	60	63	64	630	6

¹ Below 70° C, ordinary RSS had very slight surface roughness.

Die swell measured as per cent increase in outside diameter of tube compared with die.

at a rate of 7 grams per minute, with die swell 280%, in contrast to the SP RSS compound (Mooney viscosity 23) which extruded at 31 grams per minute with die swell 163%, and also extruded smoothly at the original Mooney viscosity of 55, at a rate of 21 grams per minute, die swell 270%.

These indications of greatly increased productivity for SP gum stocks, and to a lesser degree of whiting loaded stocks, under laboratory conditions have been fully confirmed in larger scale studies carried out over a wide range of conditions. Ordinary RSS and SP RSS were compared in four compounds: pure gum; 20-volume calcium carbonate loading; 50-volume calcium carbonate loading; and 30-volume china clay loading. Compounds were mixed on both open mill (42 inch) and internal mixer (No. 1 Intermix) and extruded through a 3-inch extruder. The variables examined were: compound Mooney viscosity, temperature and rate of feed, temperatures of extruder barrel and head. Four speeds of the extruder screw were used at each level of compound Mooney viscosity. Temperatures of feed stock and extruder barrel were kept at the

TABLE IV
EXTRUSIONS AT 21 RPM AND LOWEST EXTRUDABLE TEMPERATURE

Compound	Rubber	Mooney viscosity	Temp. of barrel, ° C	Throughput		Die swell, ¹ %
				lb./min	G/min	
Pure gum	SP RSS	59	110	25	380	31
	RSS	30	90	24	360	45
	SP RSS	35	70 (90)	34 (47)	340 (420)	28 (28)
50 whitening	RSS	84	60	12	160	34
	SP RSS	94	60	28	260	21
	RSS	38	60	24	320	31
	SP RSS	54	60	24	260	17
125 whitening	RSS	122	90	50	600	21
	SP RSS	140	80 (90)	46 (62)	400 (560)	13 (13)
	RSS	40	70	40	500	17
	SP RSS	55	60 (70)	51 (62)	600 (620)	11 (8)
75 clay	RSS	58	70	12	110	8
	SP RSS	78	50 (70)	20 (38)	250 (330)	3 (3)

¹ Die swell measured as for Table III.

same level and ranged from 50° to 100° C, with head temperatures 20° C higher in all cases. All extrusions were made through a tubing die of 1½-inch outside diameter and ¾-inch inside diameter.

Illustrative data are presented in Tables III to V. Table III summarizes data for the lowest extrudable temperatures and maximum screw speeds to give smooth extrusions. In Table IV data are presented for a screw speed of 20 rpm representing an average speed common in many United Kingdom factories. A

TABLE V
EXTRUSIONS AT HIGHEST TEMPERATURE EXTRUDED

Compound	Rubber	Mooney viscosity	Temp. of barrel, ° C	Max. screw speed, rpm	Max. throughput		Die swell, ⁴ %
					lb./min	G/min	
Pure gum	SP RSS	59	110	63	70	700	28
	RSS	30	100	21	31	500	45
	SP RSS	35	100	63	100	950	24
50 whitening	RSS	84	80	63	95	950	35
	SP RSS	94	80	63	118	1220	18
	RSS	38	90	63	108	1200	25
	SP RSS	54	90	63	176	1620	17
125 whitening	RSS	122	90	63	157	1704	24
			100	40	104	1140	20
	SP RSS	140	90	63	161	1640	17
			100	63	174	1580	14
	RSS	40 ²	90	63	124	1500	14
	SP RSS	55	90	63	142	1560	6
75 clay	RSS	58	90	63	104	880	6
	SP RSS	78 ³	90	63	92	670	3

¹ Surface roughened at 63 rpm due to melting of rubber at tip of die.

² Slight surface roughness.

³ At 70° C and above surface roughened with SP RSS.

⁴ Die swell measured as for Table III.

selection of results obtained at the highest extrusion temperatures is given in Table V.

Inspection of the tables shows that SP RSS invariably gives lower die swell. In the pure gum compound SP RSS shows to marked advantage on all counts, permitting extrusion at much higher compound Mooney viscosity, lower temperatures at similar compound viscosity, and faster screw speeds at all temperatures, giving greatly increased over-all productivity. With 20 volumes of whiting, increased throughput obtainable with SP RSS is still evident throughout; here, however, no lowering of extrusion temperature is possible, and faster screw speeds are possible only at the lower range of temperatures. In the presence of 50 volumes of whiting or 30 volumes of clay the use of SP RSS still results in a greater throughput, but at the lower extruding temperatures only—e.g., Table II at 20 rpm.

TABLE VI
SP BROWN CREPE TUBE EXTRUSIONS

Rubber	Compound Mooney Viscosity	Temp. of bbl. °C	Max. screw speed rpm	Throughput		Die swell, %
				Length, in./min	Wt., g./min	
White Compound		40	—	Rough Extrusion		—
2X thin		50	21 ¹	37	530	23
brown crepe	35	60	63	172	1560	17
SP brown		40	11 ²	18	300	23
crepe	51	50	63	104	1040	12
		60	63	182	1720	14
Black compound						
2X thin		40	21 ³	27	300	16
brown crepe	47	50	63	100	1000	11
		60	63	116	1100	9
SP brown		40	—	Rough Extrusion		—
crepe	68	50	63	156	1200	6
		60	63	172	1500	6

¹ Slightly rough extrusions at 40 and 63 rpm.

² Very slightly rough extrusion.

³ Very slightly rough extrusion at 21 rpm, smooth at 11 rpm. Extrusions through die 1½-inch outside diameter, 1-inch inside diameter.

Die swell measured as for Table III.

Unvulcanized sections from this program were stored over a period of 8 weeks at room temperature, and of these all the SP sections showed much less collapse than those based on ordinary RSS.

With SP rubber it is possible to use an accelerator system with a slower rate of setup than would normally be required. Thus with the system MBTS/TMTD in ratio 1/0.25, the compounds based on SP RSS containing 20 volumes of whiting or 30 volumes of clay showed greater resistance to collapse and less water-marking of tubes extruded to the same size (¾-inch outside diameter and ¼-inch inside diameter) and cured in open steam.

In Table VI are given the results of similar larger scale experiments with 2X thin brown crepe and SP brown crepe in white and black extrusion compounds of medium loading. Principal fillers in the white compound were 60 parts of activated calcium carbonate, 25 parts of titanium dioxide, and 15 parts of white factice phr, and 75 parts of MT black and 10 parts of HMF black phr in the black compound. Greater throughput for SP rubber is evident with both compounds, and the increase is substantial for the black compound. This was

confirmed in solid rod extrusions of $\frac{1}{8}$ -inch diameter, where, for instance, at 20 rpm and lowest temperature (50° C of mill and barrel) 13 to 15% increase in throughput was obtained.

Remilled crepes are often more "nervy" than first quality sheet grades and SP brown crepe may thus show to greater relative advantage than SP RSS in heavily loaded compounds. For example, an SP brown crepe compound containing 54% rubber by volume and loaded with factice, china clay, and lithopone, showed practically no die swell of a solid extrusion, in marked contrast to the 46% die swell of the corresponding compound based on 2X thin brown crepe.

TABLE VII
CALENDERING OF SP RSS

Compounds	Rubber	Mooney viscosity	Temp. range, °C	High viscosity stocks as mixed		Stocks at similar Mooney viscosity	
				Mooney viscosity	Min. temp., °C	Mooney viscosity	Min. temp., °C
Pure gum	RSS	47	90 upwards	—	—	20 to 70	80 to 100
	SP RSS	58	80 upwards	—	—	20 to 70	70 to 90
20-volume whitening	RSS	26	80 upwards	84	95	77	90
	SP RSS	36	80 upwards	94	85	78	80
50-volume whitening	RSS	41	60-70	122	90	100	90
	SP RSS	53	60-70	140	85	98	80
30-volume clay	RSS	14	60-90	58	80	58	80
	SP RSS	22	60-90	78	80	60	75

¹ Temperature range for smooth sheeting.

² Minimum temperature for smooth sheeting.

SP RUBBERS IN CALENDERING

Laboratory and larger scale experiments have been carried out to assess the relative merits of ordinary and SP smoked sheets for calendering. Although the increased shape stability of SP rubber compounds would be expected to confer some degree of advantage, the differences would not be expected to be so marked as in extrusion, since the calendered sheet is usually constrained by the liner immediately on leaving the calender.

Laboratory experiments using a 15-inch three-bowl calender indicated several advantages for SP rubbers over the corresponding ordinary grades—e.g., closer conformity to nip setting, greater regularity of thickness across the sheet and less variation with calender temperature, greater range of compound viscosity for smooth sheeting. SP rubbers should therefore be of value in obtaining smoother, more regular calendering and in controlling shrinkage—e.g., of profiled calendered sheet.

The calendering behavior of SP RSS *vis à vis* ordinary RSS was studied in greater detail using a 15 × 32 inch three-bowl Shaw calender and the four compounds of the extrusion program—viz., pure gum; 20 and 50 volumes of calcium carbonate; 30 volumes of china clay. The results are summarized in Table VII, which gives the results obtained when all the compounds were examined for smooth single nip sheeting at constant nip (0.033 inch) with calender temperatures ranging from 40° to 110° C in steps of 10° C, and feed temperatures 10 to 15° C higher than the calender roll temperatures. Inspection of Table VII shows that a lower minimum temperature for smooth sheeting is evident for

SP RSS in all the compounds. Thus the SP RSS gum compound calendered 10° C lower over a Mooney viscosity range of 20 to 70; both SP RSS whiting compounds up to 10° C lower at the two levels of viscosity studied; while the clay-loaded SP RSS compound calendered 5° C lower at the lower viscosity level—i.e., at the viscosity of the ordinary RSS compound.

The best sheeting conditions for both SP RSS and ordinary RSS were obtained at feed temperatures of the warmed up stock about 10° C above the temperature of the calender.

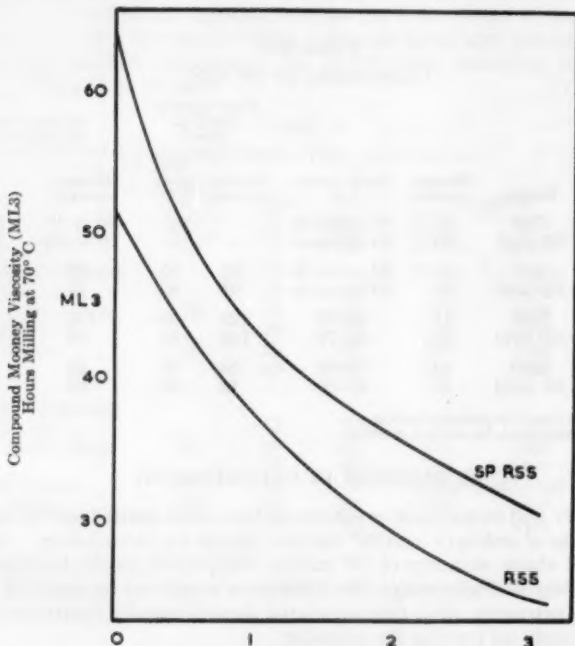


Fig. 1.—Retention of compound Mooney viscosity on milling. SP RSS and RSS in a 35 phr SRF black compound.

No differences were observed in vulcanizing the calendered sheets by conventional methods—viz., hot air cure, festooned and flat; open steam cure, bonded, wrapped, and free.

Further experiments, not shown in Table VII, were made with compounds containing 50 phr hydrated silica, in order to determine the calendering behavior of relatively high viscosity stocks. Good sheeting was obtained with SP RSS at 80° C and Mooney viscosity 90, but not at all with ordinary RSS even at Mooney viscosity 50.

Thus, in calendering the principal advantages of SP over ordinary grades lie in a 10° C lower temperature and firmer stocks. A 10° C temperature advantage could be of considerable importance in reducing heat retention of large batched up rolls, particularly when cooling facilities on the calender are lacking.

The higher compound viscosities of SP stocks result in increased firmness of the calendered sheet as it leaves the nip, assisting manipulation of stock before feeding into the liner. The slightly reduced tack of SP stocks, which does not, however, interfere with building up operations, helps to promote easy release from the liner. Proneness to blistering is reduced, as the higher viscosities of SP stocks lead to less occlusion of air in the feed. Some manufacturers have also found an advantage in reduced watermarking when SP rubber is used. SP rubber is therefore a valuable material in difficult cases such as the processing of soft compounds containing oil and white fillers.

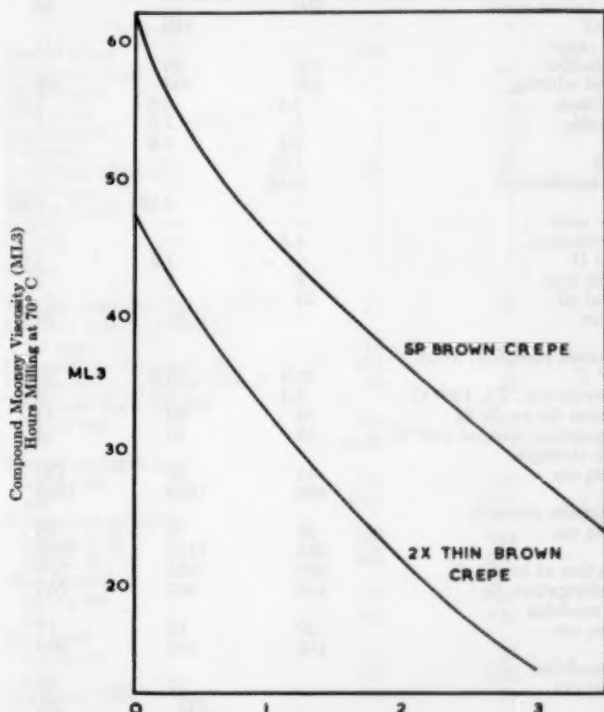


Fig. 2.—Retention of compound Mooney viscosity on milling. SP brown crepe and 2X thin brown crepe in a 75 MT/10 HAF black compound.

MOONEY VISCOSITY

The raw viscosities of SP grades of sheet and crepe fall within the normal range for corresponding ordinary grades, although SP RSS, for example, has a slightly higher raw Mooney viscosity than ordinary RSS made from the same bulking of latex and processed to sheet under similar conditions.

In the factory SP rubbers readily band on open two-roll mills, usually more easily than the corresponding ordinary grades, and the generally higher viscosities of compounds made to a fixed mixing schedule are evident by inspection of the tables.

SP compounds are also markedly more resistant to prolonged milling (Figures 1 and 2) and this is of especial value in processes involving remilling of unvulcanized compound where the use of SP rubber leads to partial or even complete elimination of waste compound. This stabilizing effect of the vulcanized particles appears more pronounced for off-grade crepe than for first quality sheet.

TABLE VIII
SP RUBBER IN A SOFT EXTRUSION COMPOUND

Compound	1	2	3
RSS (Yellow circle)	100	—	89
SP RSS	—	150	—
SP 90 crepe	—	—	111
Dark factice	100	50	—
Treated whiting	108	108	108
HAF black	2.5	2.5	2.5
Zinc oxide	5	7.5	5
Sulfur	2.4	3.6	2.4
MBTS	1.25	—	—
Other accelerators	0.43	—	—
MBT	—	2.52	1.68
Stearic acid	—	—	—
Antioxidants	1.5	—	—
Flectol H	—	1.5	1.5
Paraffin wax	3	2	3
Mineral oil	24	—	—
Vaseline	—	24	24
Compound viscosity, ML3, 212° F	20.5	33.5	35.5
Mooney scorch, T5, 120° C	3.4	4.2	5.8
Extrusion die swell, %	38	46	44
Vulcanization, min. at 140° C	15	20	15
Tensile strength			
kg/sq cm	34	96	140
psi	490	1370	1990
Aged tensile strength			
kg/sq cm	25	78	165
psi	355	1110	2350
Elongation at break, %	400	655	705
Aged elongation, %	140	465	655
300% modulus			
kg/sq cm	29	19	14
psi	415	270	200
Aged modulus			
kg/sq cm	—	37	23
psi	—	525	325
Hardness, °BS	42.5	39.5	40

Extrusion die 1-inch outside diameter, 1-inch inside diameter.

Extrusion temperatures—Barrel 50° C, head 60° C, die 70° C.

Aging period 14 days in air at 70° C.

Die swell measured as for Table II.

COMPOUNDING OF SP RUBBERS

The compounding of SP rubbers has been studied over a wide range of accelerator combinations and single accelerators in both gum and whiting-loaded stocks. With unaltered formulation SP rubbers have shorter Mooney scorch times (time to reach 5 points above the minimum viscosity at 120° C), which in almost all cases are about 70% of those for the corresponding grade of ordinary natural rubber. For single accelerator systems it is not sufficient to reduce

the amount in the compound in order to lengthen the scorch time, and if this is critical it may be necessary to use a retarder in conjunction with a suitable delayed action accelerator.

For dual accelerator systems in SP compounds a reduction in the minor component will usually effect the desired adjustment—e.g., a change of the MBTS/TMTD ratio from 1:0.25 to 1:0.125 gives similarity in the scorch behaviors of SP RSS and RSS (Yellow Circle).

TABLE IX
SP RUBBER IN A RED EXTRUSION COMPOUND

Compound	4	5	6
Brown crepe	100	—	55
SP brown crepe	—	100	—
SP 90 crepe	—	—	45
Zinc oxide	7	5.5	4.0
Stearic acid	1	0.8	0.6
Vaseline	5	5	5
Activated whiting	20	20	20
Red ochre	5	5	5
Nonox EXN	1	1	1
MBTS	1.4	1.1	0.85
TMTD	0.175	0.14	0.1
Sulfur	1.6	1.3	1.0
Mooney viscosity, ML3, 212° F	27	38	45
Mooney scorch at 120° C,			
75 min	18	16	14
Die swell on extrusion, %	131	47	23
Vulcanization, min. at 140° C	10	10	10
Tensile strength unaged			
kg/sq cm	291	251	253
psi	4140	3570	3600
Tensile strength aged			
kg/sq cm	215	190	202
psi	3060	2700	2870
Elongation at break			
Unaged, %	695	680	695
Aged, %	565	580	610
M ₁₀₀ unaged			
kg/sq cm	27	31	25
psi	380	440	355
M ₁₀₀ aged			
kg/sq cm	36	37	36
psi	515	525	515
Hardness, °BS	44	44	44

Extrusion die 1-inch outside diameter; 1/2-inch inside diameter.

Extrusion temperature—Barrel 65° C, head 80° C, die 95° C.

Aging period—14 days at 70° C in air.

Die swell measured as for Table II.

Alternatively it is often adequate to base the vulcanizing system on the unvulcanized portion of SP rubber only—i.e., 80% of the normal content of vulcanizing ingredients—in order to obtain a normal rate of cure with good physical properties and excellent performance in laboratory aging tests.

SP RUBBER AS A PROCESSING AID

While the processing advantages given by commercial grades of SP rubber are often adequate, there may be occasions when a greater measure of control

is desirable. A solution to this problem is found in a concentrated form of SP rubber—e.g., SP 90 crepe—and Tables VIII to X illustrate its use in soft rubber compounds in comparison with regular SP grades and their ordinary counterparts. Table VIII illustrates the use of SP rubbers in compounds containing large amounts of softeners. Compounds 2 and 3 are close matches to compound

TABLE X
SP RUBBER IN A BLACK EXTRUSION COMPOUND

Compound	7	8	9
RSS (Yellow circle)	100	—	55
SP RSS	—	100	—
SP 90 crepe	—	—	45
Zinc oxide	10	8	6
Stearic acid	1	0.8	0.6
Dutrex R.	4	4	4
FT black	25	25	25
HAF black	15	15	15
PBNA	1	1	1
MBTS	1.25	1	0.75
TMTD	0.325	0.25	0.2
Sulfur	1.2	1.0	0.75
Mooney viscosity, ML3, 212° F	54	68	71
Mooney scorch at 120° C,			
75 min	8	8	6
Die swell on extrusion %	62	46	24
Vulcanization, min. at 140° C	10	10	10
Tensile strength unaged			
kg/sq cm	260	253	237
psi	3700	3600	3370
Tensile strength aged			
kg/sq cm	182	198	189
psi	2590	2820	2680
Elongation at break			
Unaged, %	590	580	585
Aged, %	420	465	485
M ₂₀₀ unaged			
kg/sq cm	68	66	68
psi	970	940	970
M ₂₀₀ aged			
kg/sq cm	100	94	84
psi	1420	1340	1200
Hardness, °BS	56	56	57

Extrusion die $\frac{5}{8}$ -inch outside diameter, $\frac{1}{8}$ -inch inside diameter.

Extrusion temperature—Barrel 65° C, head 80° C, die 95° C.

Aging period—14 days at 70° C. in air.

Die swell measured as for Table II.

1 for processing performance while giving much firmer stocks, and for hardness of the vulcanizate. In addition, physical properties and their retention on aging are greatly improved.

Compounds 6 and 9 containing SP 90 crepe (Tables IX and X) contain twice as much SP vulcanized component as those based on the regular SP grades (Nos. 5 and 8). The relative processing performances of the compounds of Tables IX and X are illustrated in Figure 3 for extruded tubing after unsupported vulcanization in open stream.

A particular advantage of the concentrated form of SP rubber is that it can be added to any grade of natural, or suitable type of synthetic rubber, thereby

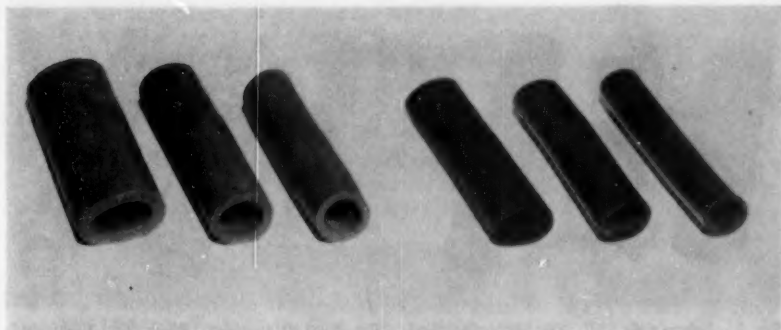


FIG. 3.—Left to right. Red tubing compounds 4, 5, 6; black tubing compounds 7, 8, 9. Left to right in each. Ordinary rubber, SP rubber, SP 90 crepe in amount to give a greater degree of SP properties.

greatly increasing the flexibility of SP rubber usage. It is desirable that the concentrated form of SP should be capable of direct addition to the internal mixer with the other rubber of the compound. The adoption of this technique with the SP 90 crepe used in the experiments described below resulted in some loss of surface finish of extrusions—e.g., Figure 3. Unless otherwise indicated, the material was given a preliminary breakdown on a cool mill, and when this was done extremely smooth surface finish was obtained. The objective of smooth surface finish to extruded or calendered compounds when SP concentrate is added direct to the internal mixer at the commencement of mixing has since been achieved by the Rubber Research Institute of Malaya with a modified material.

Blends of SP 90 crepe with grades of natural rubber in the appropriate proportions possess similar processing properties to regular SP grades of sheet and crepe. In comparison with crosslinked SBR (SBR 1009 types), SP 90 crepe has a more pronounced effect on the processing properties of both NR and SBR for both decreased die swell and increased surface smoothness of extrusions. The relative effects of SP 90 crepe and SBR 1009 on surface smoothness are illustrated in Figure 4 for RSS and Figure 5 for SBR (cold, nonstaining) in

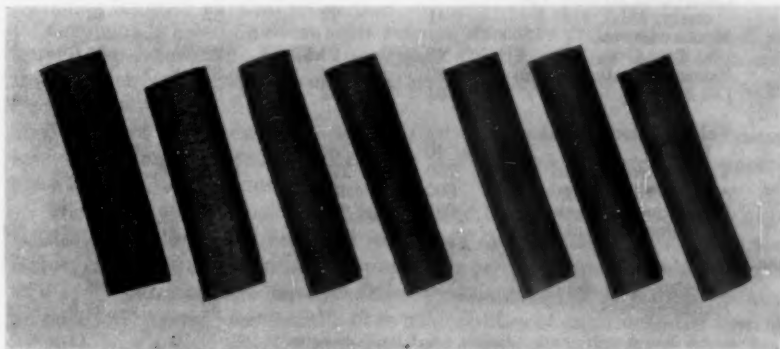


FIG. 4.—Left to right. RSS, RSS with 10, 20, 30, crosslinked SBR 1009, RSS with 10, 20, 30 SP 90 crepe.

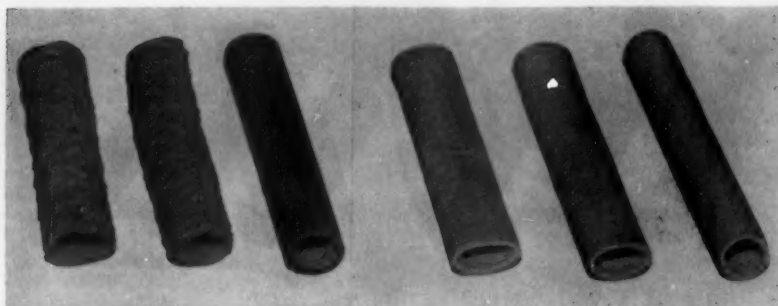


Fig. 5.—Left to right SBR 1500; SBR/crosslinked SBR, 50/50; SBR/SP 90 crepe, 50/50.

Fig. 6.—Left to right. White filled Compounds 10, 11, 12 based on SBR (10); SBR/crosslinked SBR 100, (11); SBR/SP 90 crepe, (12).

TABLE XI

BLENDS OF SBR WITH CROSSLINKED SBR AND SP GRADES OF NR IN A WHITE LOADED COMPOUND FOR EXTRUSION

	Compound No.			
	10	11	12	13
SBR 1500	100	75	75	50
SBR 1009	—	25	—	—
SP crepe	—	—	—	50
SP 90 crepe	—	—	25	—
Zinc oxide	15	15	11.6	13.5
Stearic acid	1	1	0.77	0.9
Devolite clay	50	50	50	50
Precipitated whiting	25	25	25	25
Titanium dioxide	10	10	10	10
Coumarone resine	10	10	10	10
Paraffin wax	5	5	5	5
Sulfur	2	2	1.55	1.8
MBTS	1.2	1.2	0.93	1.1
TMTD	0.15	0.15	0.12	0.13
Compound Mooney viscosity, ML3, 212° F	41	32	52	40
Mooney scorch, T_5 at 130° C	28.5	24.5	22	25.5
Extrusion rate, cm/min	82	77	80	111
Die swell, %	81	82	64	64
Vulcanization, min at 153° C	40	40	20	20
Tensile strength, psi	750	725	1080	1720
Aged tensile strength, psi	600	480	1240	970
Elongation at break, %	695	650	760	665
Aged elongation at break, %	520	440	615	490
300% modulus, psi	215	250	265	420
Aged 300% modulus, psi	355	340	355	485
Hardness, °BS	54	53	52	53.5

Extrusion die— $\frac{1}{8}$ -inch outside diameter, $\frac{1}{16}$ -inch inside diameter.

Extruder temperatures—Barrel 65° C; head 85° C; die 95° C. Screw speed, 40 rpm.

Aging 14 days in air at 70° C.

Die swell measured as for Table II.

pure gum compounds. The good surface finish obtained with the SBR/SP 90 crepe blend of Figure 5 is associated with greatly improved physical properties—viz., tensile strength 1350 psi and breaking elongation 530%.

These results are of considerable interest, as they indicate the potentialities of such blends in white loaded SBR compounds. This use of SP 90 crepe is illustrated in Figure 6 and Table XI, showing the resulting improvement in surface finish, lower die swell, and resistance to collapse of thin-walled tubing, coupled with improved physical properties before and after accelerated aging. In this instance the SP 90 crepe was added direct to the internal mixer without prior mastication.

SP 90 crepe and crosslinked SBR were further evaluated in four series of black compounds of hardness about 55° BS based on RSS(YO) and SBR 1400. These contained four different blacks in loadings of 60 MT, 30 FEF, 25 HAF, and 25 MPC black phr. In each series SP 90 crepe previously broken down on a cool mill, and crosslinked SBR 1009 were added at 20-phr level.

In the compounds based on RSS(YO) SP 90 crepe performed similarly to SP RSS for die swell and surface smoothness of solid rod extrusions.

Under the fixed conditions of extruder temperature and screw speed SP 90 crepe showed greater power of conferring surface smoothness and lower die swell than SBR 1009 in both types of compounds. Thus under conditions of smooth or nearly smooth extrusion, as with FEF black, SP 90 crepe gave about 30% reduction in die swell with both NR and SBR, in contrast to SNR 1009 which gave a zero reduction in NR and about 15% reduction in SBR.

The addition of SP 90 crepe raised the average tensile strength of the SBR compounds by 20%, whereas SBR 1009 gave no improvement. In each case average retention of tensile strength on aging was about 85%.

Average tensile strengths of RSS(YO) compounds containing SP rubber or SBR 1009 were very similar, the former being 90% and the latter 85% of the average tensile strength of RSS(YO). Retention of tensile strength on aging was 75% for RSS(YO) compared with 80 to 85% for compounds containing SP rubbers or SBR 1009.

SUMMARY

SP rubbers give greater latitude in extrusion and calendering processes by extending the range of operating conditions and giving greater scope for compounding for good physical properties.

Compounds based on SP rubbers extrude smoothly with lower die swell at lower temperatures and higher viscosities. Greater productivity is obtained through the faster screw speeds which are possible with SP rubbers in many types of compound.

SP rubber compounds calender with greater conformity to gage, greater ease of handling and control of shrinkage of the calendered sheet, at temperatures 10° C lower than normal.

The firmer stocks given by SP rubbers and their greater resistance to degradation on milling lead to reduced wastage of unvulcanized compound in the factory, while the stricter control of processing permitted by SP rubbers results in a lower percentage of rejected articles. Evaluation of an experimentally produced SP 90 crepe has indicated the potentialities of a concentrated form of SP rubber as a more efficient processing aid than crosslinked SBR 1009 with NR and SBR.

ADDENDUM

Since this paper was written, SP 90 crepe, described in the section "SP rubber as a processing aid" has been replaced by an improved material (see page 819) known as PA 80^{9,10}.

PA 80 is readily blended with other rubber, and requires no further treatment before use (unlike SP 90).

PA 80 may be used on open mills and in internal mixers. In both cases the simplest and most effective method is to add PA 80 along with the other rubber at the start of operations. In internal mixers this is conveniently at the commencement of the premastication schedule.

The examples given for the properties and uses of SP 90 are applicable to PA 80, although the compound details require to be slightly modified to allow for the different composition of PA 80 (80 instead of 90 per cent crosslinked rubber).

ACKNOWLEDGMENT

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REFERENCES

- ¹ Baker, H. C., *Trans. Inst. Rubber Ind.*, **32**, 77 (1956).
- ² British Insulated Callenders Cables, Ltd., Brit. Patents 755,553, 755,567.
- ³ Rubber Research Inst. of Malaya, *Planters' Bulletin*, 1957, No. 32, 83.
- ⁴ Brit. Patent 803,013.
- ⁵ Sekhar, B. C. and Drake, G. W., *J. Rubber Research Inst. Malaya* **15**, 216 (1958).
- ⁶ Fletcher, W. F. and Baker, H. C., BRPRA Technical Bulletin No. 2, S.P. Rubber, with Additional Information Sheets A and B.
- ⁷ Baker, H. C., *Rubber Developments* **8**, 70 (1955); **10**, 127 (1957).
- ⁸ Baker, H. C., *Rubber J. and Intern. Plastics* **136**, 615 (1959).
- ⁹ Anon, *Planters' Bulletin, Rubber Res. Inst. of Malaya*, 1960, No. 47.
- ¹⁰ Baker, H. C., *Rubber Developments*, 1960, Spring issue.

POLYMERIZATION OF VINYL MONOMERS IN RUBBER LATEXES

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In recent years numerous workers have reported on the polymerization of vinyl monomers, in the presence of polymers, in which graft copolymers and/or homopolymers are formed. Kinetic studies of such reactions have been relatively few, however, particularly for systems involving polymer latexes rather than solutions. In the present paper a kinetic study of the polymerization of styrene, methyl methacrylate, and homologous methacrylic esters in natural rubber latex is reported, and certain abnormal features of the polymerizations are discussed.

EXPERIMENTAL

Materials.—The natural rubber latex used was a centrifuged concentrate, initially of 60% dry rubber content (DRC) and preserved with ammonia. In all experiments, the latex was diluted to the required DRC with distilled water and further stabilized by the addition of sufficient potassium laurate to give a concentration of 0.5% of the soap on the weight of diluted latex. The pH was adjusted to approximately 11.0 with potassium hydroxide, and ammonia and dissolved oxygen were then completely removed by blowing nitrogen through the latex at 50° C for 72 hours.

The monomers were obtained from commercial sources and were distilled before use.

The azobisisobutyronitrile (AZBN) and ammonium persulfate used as catalysts were of laboratory reagent grade.

Methods.—Rates of polymerization were measured using a dilatometer (Figure 1), based on a design by Burnett¹, which contained about 50 ml. of latex confined over mercury. Volume changes of less than 1 part in 10⁶ could be detected by means of an automatic recorder. An air thermostat surrounding a thermostated oil bath enabled the latter to be controlled to better than $\pm 1 \times 10^{-3}$ ° C at 50° C, the temperature at which many of the polymerizations were carried out. The dilatometer in detail elsewhere². In experiments with methyl methacrylate at 50° C, the relation between monomer conversion and volume contraction was measured gravimetrically and found to be in excellent agreement with that calculated from density data. For the other monomers, percentage conversion was calculated using the density data given in the literature.

In carrying out a polymerization, the monomer was added to the diluted and deammoniated latex in a vessel which was flushed out with nitrogen and then rotated end over end for 2 hours at room temperature to ensure thorough mixing. The mixture was then heated to a temperature a few degrees higher than the polymerization temperature before being admitted to the dilatometer,

which had been allowed to equilibrate in the thermostat. If AZBN was used as catalyst, it was dissolved in the monomer before adding the latter to the latex; with persulfate as catalyst, it was added as a preheated aqueous solution to the latex-monomer mixture immediately prior to filling the dilatometer.

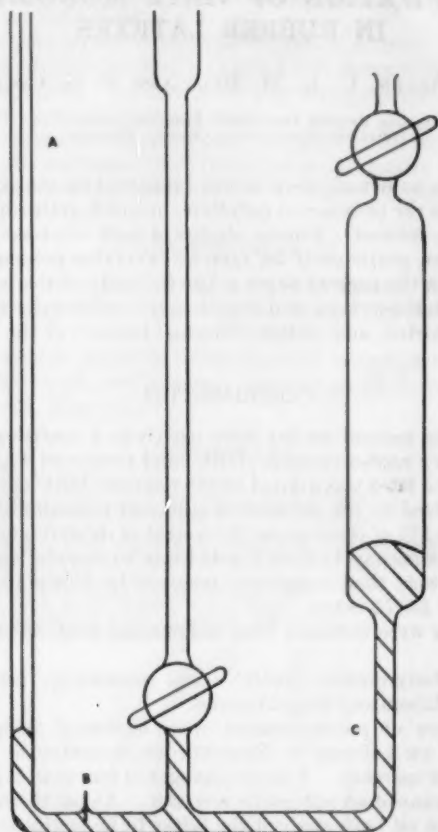


FIG. 1.—Diagram of dilatometer. A., veridia tubing, 0.7-mm; B, platinum wire contact; C, ~6-mm internal bore.

RESULTS AND DISCUSSION

Effect of catalyst concentration.—Haward³ and Smith and Ewart⁴ have considered the case of polymerization in aqueous dispersions containing a fixed number of monomer-polymer particles in which polymerization is initiated by water-soluble catalysts. It was shown that if the particles were so small that the number of growing polymer radicals per particle at any time was either one or zero, then the rate of polymerization should be independent of the catalyst concentration, $[C]$. If, however, the catalyst concentration is sufficiently

high, more than one polymer radical may exist even in small particles in which case the rate would be proportional to $[C]^1$, as in a bulk polymerization.

With catalysts insoluble in water but soluble in the monomer-polymer particles, and which decompose so that each catalyst molecule forms two initiating radicals, it has been shown by van der Hoff⁶ that the rate of polymerization should be proportional to $[C]$ at low catalyst concentrations, provided that the monomer-polymer particles are sufficiently small. At higher catalyst concentrations the rate should be proportional to $[C]^1$ irrespective of particle size.

Typical conversion-time plots for the polymerization of methyl methacrylate or styrene in rubber latex are shown in Figure 2. With both monomers there is an induction period which decreases with increasing catalyst concentration. Figure 3 shows the dependence of \log (maximum rate) on $\log [C]$ for

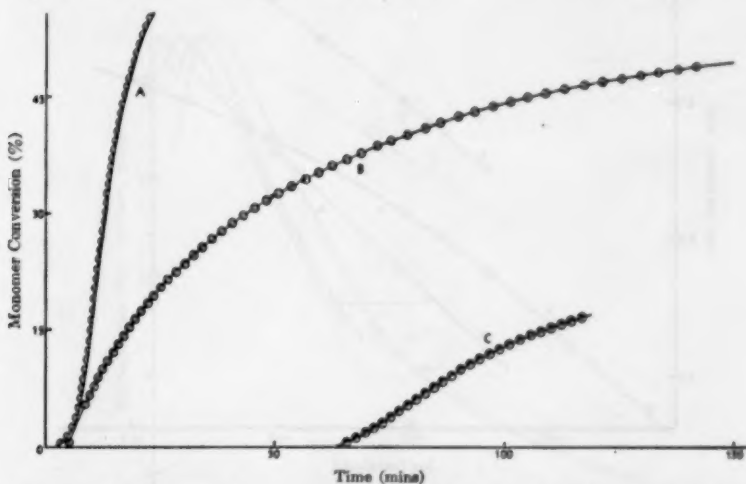


Fig. 2.—Rates of polymerization of methyl methacrylate and styrene in rubber latex (DRC = 5%), in presence of ammonium persulfate (0.08% on latex). Initial weight ratio of monomer to rubber = 1:1. A, Styrene at 70°C; B, Methyl methacrylate at 70°C; C, Methyl methacrylate at 50°C.

methyl methacrylate polymerizations at 50°C. With AZBN as catalyst, concentrations corresponding to more than about 5% on the weight of monomer could not be used because of its limited solubility in methyl methacrylate, but up to this concentration the monomer-soluble AZBN gives the same shape of curve as does the water-soluble ammonium persulfate. Indeed, the two curves can be made to coincide closely by dividing the AZBN concentration by the factor 2.9 (Figure 3).

It can be seen that at low catalyst concentrations the maximum rate of polymerization is proportional to $[C]$, while at higher concentrations (in the absence of benzene) there is a transition to an approximately half-order dependency. If, however, the monomer is diluted with an equal weight of benzene before addition to the latex so as to give a 1:1:1 proportion of benzene, methyl methacrylate, and rubber, then the maximum rate is proportional to $[C]$ over the whole range of ammonium persulfate concentration studied (Figure 3).

The results using ammonium persulfate as catalyst at low concentrations show that the system does not obey small particle Smith-Ewart kinetics. This is not surprising, because natural latex contains many particles greater than 0.5 microns in diameter which account for a high proportion by weight of the rubber, and which are considerably larger than the particles usually formed in emulsion polymerizations. The lack of agreement with Smith-Ewart theory is presumably due to the latex containing more than one growing radical per particle.

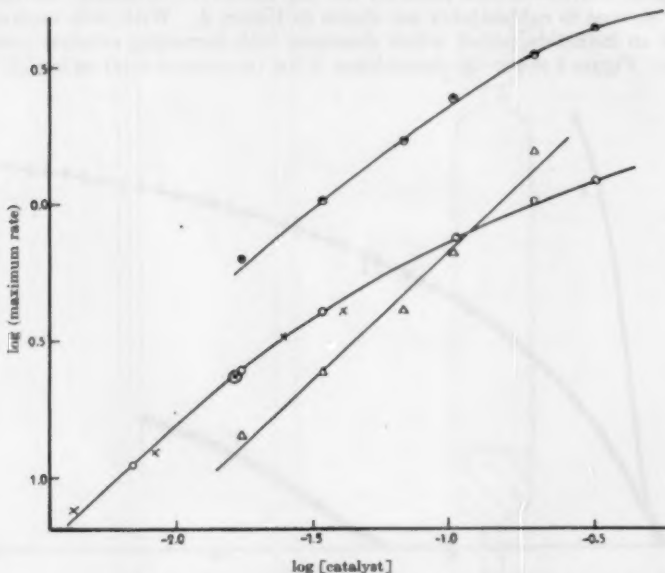


FIG. 3.—Effect of catalyst concentration on rate of polymerization (maximum) of methyl methacrylate in rubber latex (DRC=5%) at 50° C. ○ Initial weight ratio of monomer to rubber =1:1; persulfate catalyst. ● Initial weight ratio of monomer to rubber =2:1; persulfate catalyst. × Initial weight ratio of monomer to rubber =1:1; AZBN catalyst. △ Initial weight ratio of monomer to rubber to benzene =1:1:1; persulfate catalyst.

The first-order dependency of maximum rate on catalyst concentration at low values of $[C]$, and the subsequent transition to half-order dependency, is consistent with a monomolecular termination step which predominates at low rates of initiation but which is unimportant at high rates of initiation, where a normal bimolecular termination reaction predominates. The most likely cause of monomolecular termination would be the formation of an inactive radical by chain transfer, although a physical inactivation of the growing radicals by some occlusion process is conceivable. When benzene is present in the monomer-swollen rubber particles, the monomolecular termination step apparently predominates over the whole range of persulfate concentrations used.

The efficiencies, f_A and f_B , of AZBN and persulfate in initiating the polymerization of methyl methacrylate under the conditions referred to in Figure 3 are readily calculated.

For the same rates of initiation,

$$2 k_A f_A [\text{AZBN}] = 2 k_B f_B [\text{persulfate}]$$

where k_A and k_B (the rate constants for thermal decomposition of the catalysts) are $2.6 \times 10^{-6} \text{ sec.}^{-1}$ and $1 \times 10^{-6} \text{ sec.}^{-1}$, respectively^{6,7}. Since, from Figure 3,

$$\frac{[\text{AZBN}]}{[\text{persulfate}]} = 2.9$$

$$\frac{f_B}{f_A} = 7.5$$

If all the radicals derived from persulfate do not enter the latex particles, their relative efficiency compared with AZBN would be even higher. The lower

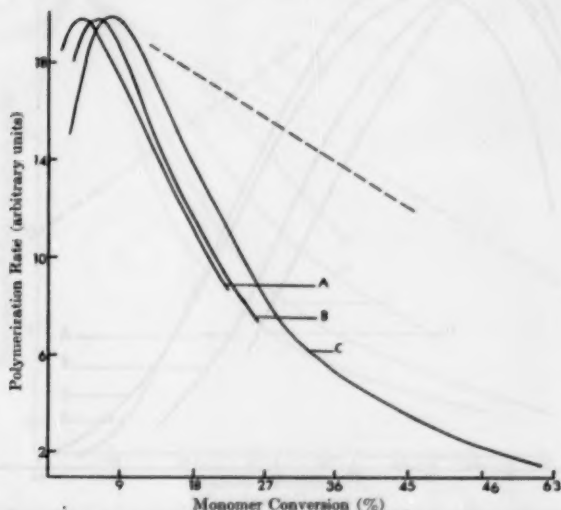


FIG. 4.—Dependence of polymerization rate on percentage conversion of methyl methacrylate in rubber latex (DRC=5%) at 50° C. Initial weight ratio of monomer to rubber = 1:1. Catalyst, ammonium persulfate. A, 0.08% catalyst; B, 0.23% catalyst; C, 0.77% catalyst.

efficiency of the radicals from AZBN may be due to the high viscosity of the latex particles producing a cage effect which reduces the effective decomposition rate of AZBN.

It has been assumed that polymerization outside the latex particles was negligible, even with water-soluble persulfate as catalyst. At the concentrations of potassium laurate used, very few micelles should be present in which homopolymerization of monomer could be initiated. The fact that two of the curves in Figure 3, using AZBN and persulfate as catalysts, can be superimposed is also evidence for the correctness of the above assumption.

Variation of rate with monomer conversion.—Figures 4–6 show the variation in rate of polymerization with the percentage conversion of methyl methacrylate in latexes containing the monomer and rubber in initial proportions of 1:1 and 2:1 by weight, and in latex containing a 1:1:1 ratio of benzene, methyl metha-

crylate, and rubber. All the plots show a maximum at low conversion. In Figures 4 to 6 the curves have been displaced vertically to give the same maximum rate in order to compare their shapes. The most interesting feature of the curves is the very rapid decrease in rate after the maximum has been reached. In the absence of benzene, the rapid decrease in rate commences at slightly lower monomer conversions as the concentration of persulfate is reduced, but the effect is not marked. It will be noted that a very similar rapid decrease in rate occurs using AZBN as catalyst. The extent to which the reduction in monomer concentration alone would be expected to decrease polymerization rate, if the system were homogeneous and obeying steady state kinetics, is indicated by the broken lines in Figures 4 to 6.

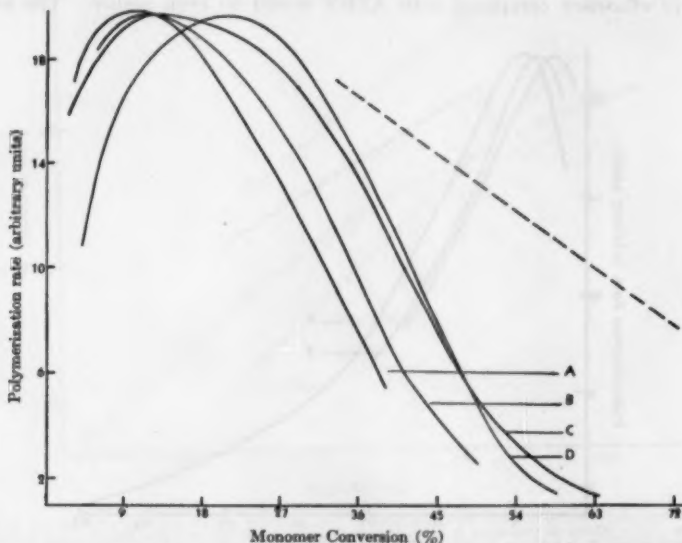


FIG. 5.—Dependence of polymerisation rate on percentage conversion of methyl methacrylate in rubber latex (DRC=5%) at 50° C. Initial weight ratio of monomer to rubber =2:1. Catalyst, ammonium persulfate or AZBN. A, 0.04% persulfate; B, 0.16% persulfate; C, 0.46% persulfate, D, 0.28% AZBN.

It is well known that in the later stages of the bulk polymerization of methyl methacrylate and certain other monomers, the termination and propagation steps become diffusion controlled because of the great increase in viscosity of the system. It was considered possible from the data of Figure 4, that the increase in rate to a maximum was due to a reduction in the rate of termination of the polymer radicals or a slow attainment of a steady state while the subsequent rapid decrease in rate was caused by diffusion control of the propagation step. The experiments in the presence of benzene (Figure 6) do not support this simple view. The rapid decrease in rate, instead of starting at a higher conversion, begins at almost exactly the same conversion as in the absence of benzene, although the viscosity of the latex particles must be very different, provided they are homogeneous. However, the strong tendency of mixtures of polymers to separate forming heterogeneous systems suggests that the growing

polymethyl methacrylate chains will aggregate within the latex particles and a slow rate of diffusion of monomer into these aggregates might account for the rapid decrease in polymerization rate. Although we would expect the rate of diffusion of monomer into such aggregates to increase if they were "swollen" with benzene, this effect could be counterbalanced by the more ready formation of aggregates due to the viscosity of the latex particles as a whole being reduced.

As further evidence to check the above ideas, determinations of the rates of polymerization as a function of percentage conversion were carried out with different monomers and at different temperatures. The additional monomers chosen were ethyl methacrylate and butyl methacrylate, whose polymers have second-order transition temperatures (T_g) of approximately 65° and 20° C, respectively, as compared with 100° C for polymethyl methacrylate. It was

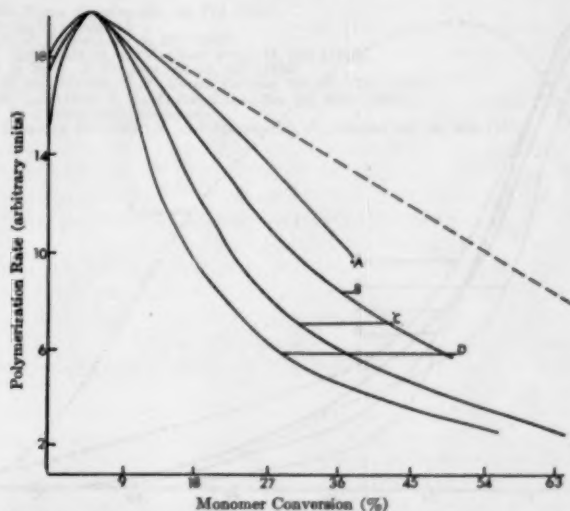


FIG. 6.—Dependence of polymerization rate on percentage conversion of methyl methacrylate in rubber latex (DRC = 5%) at 50° C. Initial weight ratio of monomer to rubber in benzene = 1:1:1. Catalyst, ammonium persulfate. A, 0.08%; B, 0.16%; C, 0.23%; D, 0.46%.

anticipated that polymerization at temperatures below T_g would give rate-conversion curves closely resembling in shape those of methyl methacrylate at 50° or 70° C, and that above T_g the decrease in rate with increasing conversion would be much less rapid. In fact, Figure 7 shows that the rate-conversion curves were very similar in shape for all three methacrylates, whether the temperature of polymerization was above or below T_g . It can be argued that since the polymer aggregates will be swollen with monomer, the transition temperature of the aggregate will be lower than that of the pure polymer. Nevertheless, there is so little difference between the curves for methyl methacrylate at 50° C (50° C below T_g for polymethyl methacrylate) and for butyl methacrylate at 70° C (50° C above T_g for this polymer) that simple diffusion of monomer into the aggregates is very unlikely to be the rate-determining step in the polymerization.

Strong evidence that aggregation of growing polymethyl methacrylate

chains does occur within the latex particles, to form microaggregates, has been obtained in these laboratories⁸ from studies on the swelling behavior and the mechanical properties of films of natural latex in which methyl methacrylate has been polymerized. Cooper et al.⁹ also invoked the idea of the formation of microaggregates of polymethyl methacrylate in rubber latex particles to account for certain aspects of the radiation-induced polymerization of methyl methacrylate. It will be seen from Figure 7 that although the methacrylates all give very similar rate-conversion curves, the one for styrene shows a maximum at an appreciably higher conversion, and the rate then decreases more slowly than in the systems containing methacrylates. If polymerization in the surrounding rubber phase is rapid compared with the rate of polymerization in the microaggregates of the polymer, the observed rate would clearly depend on the partition

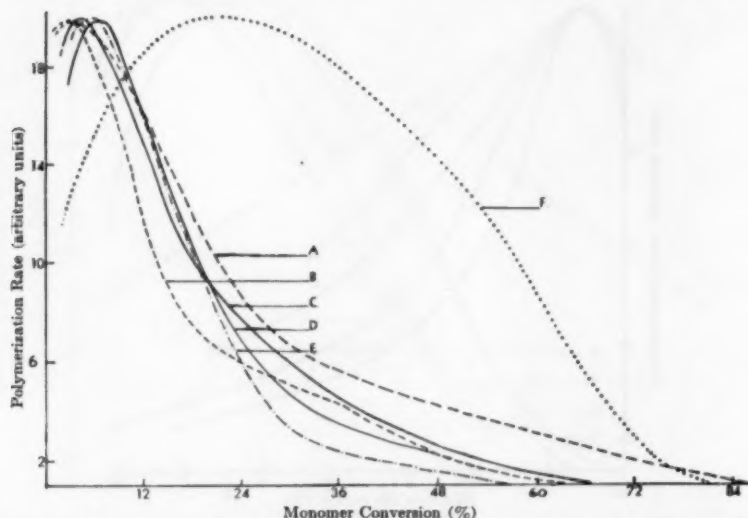


FIG. 7.—Dependence of polymerization rate on percentage conversion of different monomers in rubber latex (DRC = 5%). Initial weight ratio of monomer to rubber = 1:1. Catalyst, ammonium persulfate. A, Ethyl methacrylate, 50° C; B, Ethyl methacrylate, 70° C; C, Methyl methacrylate, 70° C; D, Methyl methacrylate, 50° C; E, Butyl methacrylate, 70° C; F, Styrene, 70° C.

of monomer between the rubber phase and the microaggregates. Because the solubility of alkyl methacrylates in their own polymers is much greater than in rubber, an abnormally rapid decrease in over-all rate with increasing conversion would be expected. With monomers such as styrene whose solubility in rubber is more comparable with the solubility in its own polymer, the decrease in rate should be less marked. Furthermore, aggregates of polystyrene in rubber will probably not be formed so readily as aggregates of the more polar alkyl methacrylate polymers, so that any abnormal decrease in rate for styrene polymerization should occur at higher conversions compared with the methacrylates.

The results with styrene (Figure 7) are in accord with these views. Actually, the decrease in rate for styrene from the point of maximum rate to about 60% conversion is little different from that to be expected as a result of depletion of monomer by reaction in a homogeneous system. For the alkyl metha-

crylates, however, we consider that the preferential absorption of monomer by microaggregates of the polymer in which polymerization is slow, compared with the rate in the surrounding rubber phase, provides the best explanation for the experimental data. The slow polymerization in the microaggregates is apparently not due to diffusion control of the polymerization, but it might be accounted for by a lower rate of initiation within the aggregates.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Burnett G. M., *Trans. Faraday Soc.* **46**, 772 (1950).
- ² Bell, C. L. M., to be published.
- ³ Haward, R. N., *J. Polymer Sci.* **4**, 273 (1949).
- ⁴ Smith, W. V. and Ewart, R. H., *J. Chem. Phys.* **16**, 592 (1948).
- ⁵ van der Hoff, B. M. E., *J. Polymer Sci.* **33**, 487 (1958).
- ⁶ Bawn, C. E. H. and Mellish, S. F., *Trans. Faraday Soc.* **47**, 1216 (1951).
- ⁷ Kolthoff, I. M. and Miller, I. K., *J. Am. Chem. Soc.* **73**, 3055 (1951).
- ⁸ Mumford, R. B., private communication.
- ⁹ Cooper, W., Vaughan, G., Miller, S. and Fielden, M., *J. Polymer Sci.* **34**, 651 (1959).

VULCANIZATION OF ELASTOMERS. 26. VULCANIZATION OF NATURAL AND SYNTHETIC RUBBERS BY SULFUR IN THE PRESENCE OF ORGANIC BASES.

II *

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INTRODUCTION

Some time ago we reported on the course of vulcanization of natural rubber by sulfur¹ in the presence of organic bases, especially DPG (diphenylguanidine), as accelerators². It appeared then that the sulfur concentration decreases at all temperatures and all accelerator concentrations according to a time law of fractional order, $n = 0.7$ to 0.75 . An activation energy of 30 kcal/mole was calculated through the temperature dependence of the rate constant for a reaction of order 0.7. The rate of decrease of the sulfur concentration was dependent upon the particular constitution of the base which was present in the rubber mixture. A concordance between rate and dissociation constant of the base, which has frequently been emphasized, was verified.

Particularly interesting, however, was the characteristic dependence of the rate constant for disappearance of sulfur upon the DPG content of the rubber compound when the initial sulfur concentration was constant. After an initial rise which was practically linear, the rate constant passed through a transition range where it increased more slowly and finally became independent of DPG content, that is, it became practically constant.

Meanwhile, we had found similar relationships in vulcanizations which were accelerated by CBS (N-cyclohexyl-2-benzothiazolylsulfenamide¹); and Cherubim³ was able to demonstrate a similar course for the rate constant of sulfur disappearance in vulcanizations accelerated with aniline. Furthermore, corresponding observations were made by Lorenz and Echte⁴ when vulcanizates containing MBT (mercaptobenzothiazole), zinc oxide and zinc stearate were more closely studied.

The above kinetic results were correlated by us with the formation of an intermediate compound by the accelerator and sulfur, which was considered to be the true vulcanizing agent. Because of the significance for the knowledge of the fundamentals of vulcanization if we could find confirmation for the formation of intermediate reaction products during accelerated vulcanizations, we made an extended, thorough study of the vulcanization of Perbunan N 2818 by sulfur in the presence of DPG, and investigated carefully the course of the initial rate of sulfur disappearance with the initial concentration of sulfur. This had not been done in corresponding studies made with natural rubber².

DISCUSSION OF RESULTS

The starting material was Perbunan N 2818 which had been exhaustively extracted with methanol. It was then processed and vulcanized as has al-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe from *Kautschuk und Gummi*, Vol. 12, WT 205-211, August 1959. Tables of data have been omitted to save space.

ready been described a number of times. For the quantitative determination of the unreacted free sulfur, the vulcanizates were extracted at room temperature with benzene/alcohol, with repeated renewal of the extractant. The sulfur in the extracts was converted to KSCN by means of KCN and the solutions titrated conductometrically with AgNO_3 after suitable preparation. The DPG which was still present was determined quantitatively by an acidimetric conductivity titration on the extract.

Temperature-dependence of the decrease in sulfur.—We first studied the decrease in sulfur concentration at various temperatures in the range from 100° to 130°C . In this work, 100 g of the Perbunan mixture contained 10 mmoles of DPG and 10 mmoles of S_8 .

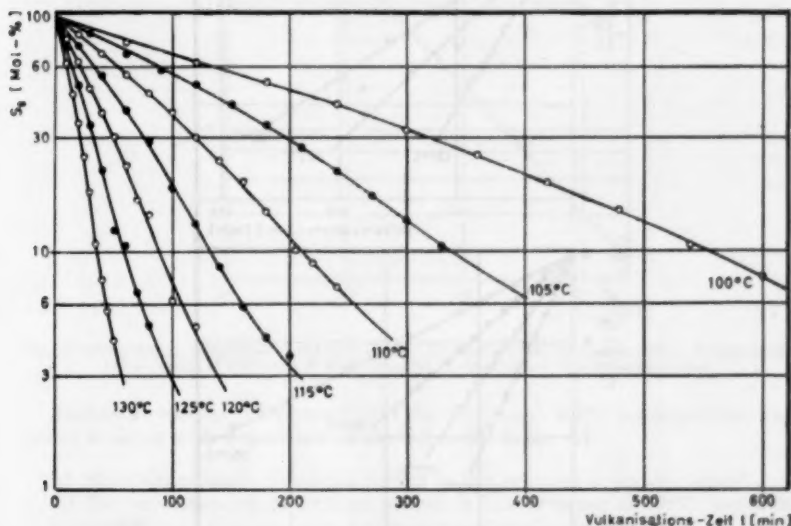


FIG. 1.—Decrease in sulfur concentration plotted as a first order reaction for a Perbunan N 2818 vulcanizate with 10 mmoles S_8 and 10 mmoles diphenylguanidine in 100 g mixture, at various temperatures. Ordinate: As given. Abscissa: Vulcanization time, t (min).

Figure 1 shows the decrease in sulfur, the analytical data being plotted as if coming from a first order reaction. The curves are concave for the greater part of the reaction range; below a reaction of 80 to 90 per cent, they show a point of inflection and continue with convex curvature. From this we must conclude that a time law of the first order—as is also true for other cases of accelerated vulcanizations^{1, 2}—is not exactly followed. Since the curves in by far the greater range of the reaction have a concave curvature, the reaction order in this range must be less than one.

It should be emphasized here that the slight waviness of the curves is not noticed when we examine only a narrow range of the decrease in sulfur concentrations; furthermore, the choice of the scale for the abscissa is not without significance in judging the shape of the curves, in case the graphical method of evaluation is used exclusively. The recognition of the actual circumstances should be most certain when—as is done here—we carefully examine a whole group of curves.

A careful study⁵ of the curves of Figure 1 showed the reaction to be of order 0.8; the same value is found in vulcanizations of Perbunan in the presence of CBS¹. In fact, as is shown in Figure 2, straight lines are always obtained over the greater part of the run of sulfur decrease, when the expression $[1/(1 - 0.8)](a - x)^{1-0.8}$ is plotted against the time of vulcanization (a = initial concentration of sulfur, S_0 , and x = the reacted fraction, S_t). Of course, this time law does not hold over the whole reacting range, because, as is shown in Figure

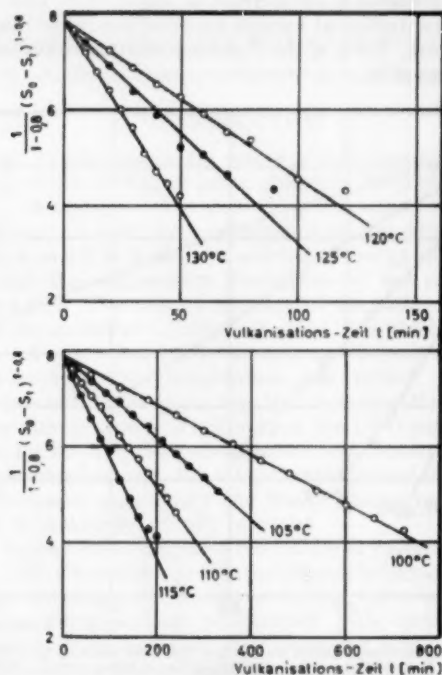


Fig. 2.—Decrease in sulfur concentration plotted as an 0.8 order reaction for a Perbunan N 2818 vulcanizate with 10 mmoles S₈ and 10 mmole diphenylguanidine in 100 g mixture at various temperatures. Ordinate: As given. Abscissa: Vulcanisation time, t (min).

1, the curves show points of inflection close to the end of the reaction. Yet the representation of experimental results as belonging to the order 0.8 is very close to the actual relationship.

When we plot the logarithm of the rate constant against the reciprocal of the temperature, we obtain the straight lines of Figure 3, from whose slopes an activation energy of 28 kcal/mole is calculated. This is in good agreement with values which we have frequently found in the past for accelerated vulcanizations.

Dependence of the rate of sulfur decrease on the initial concentrations of DPG and of sulfur.—The falling off of the sulfur concentration according to a fractional order of reaction ($n = 0.7$ to 0.8) at all temperatures, seems from our experience to be characteristic of a series of accelerated sulfur vulcanizations; and in many cases we could produce evidence that the order of reaction was

independent of the initial concentration of the reactants (accelerator and sulfur). Probably we may conclude from these results that there is a fundamental similarity in many vulcanization processes, which despite all the individuality of such processes, is expressed in the kinetics of the sulfur decrease.

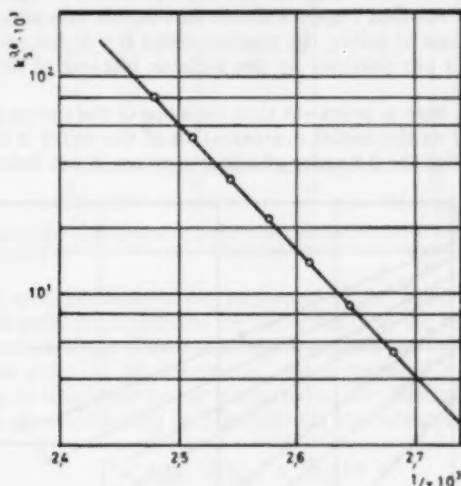


Fig. 3.—Temperature dependence of the rate constant for the 0.8 order reaction for sulfur decrease in the vulcanization of Perbunan N 2818 by sulfur in the presence of diphenylguanidine.

Hence, we can say in summary that the decrease in sulfur concentration was found to agree with a time law of the 0.7 to 0.8 order in:

- a) the vulcanization of natural rubber in the presence of organic bases²
- b) the vulcanization of natural rubber in the presence of DPG and zinc oxide⁶
- c) the vulcanization of Perbunan in the presence of sulfenamide¹
- d) frequently, but not always, the vulcanization of natural rubber and of Perbunan in the presence of benzothiazolyl disulfide⁷
- e) according to recent studies by Scheele and Echte⁸, the vulcanization of natural rubber in the presence of MBT and zinc oxide.

It may now be pointed out that in these vulcanization reactions, in which the activation energy for sulfur decrease (temperature coefficient of the rate) is generally 28 to 30 kcal/mole, there is another peculiar characteristic to which Lorenz and Echte⁹ have referred in connection with their studies of vulcanizations accelerated by mercaptobenzothiazole in the presence of zinc oxide and zinc stearate. It consists of a discrepancy in the reaction order from the standpoint of time and concentration, which is noticed when the kinetics of the sulfur decrease at various initial concentrations of accelerator and sulfur is studied closely. The complex nature of accelerated sulfur vulcanizations is clearly reflected in the results thus obtained.

We therefore studied carefully what happened to the rate of decrease in sulfur when the DPG content was held constant at 10 mmole in each 100 g

Perbunan while the initial concentration of sulfur was raised stepwise from 5 to 35 mmoles of S_8 . This study gave the opportunity to prove if the reaction order was independent of concentration or not. The explanation of an order of reaction is a formality to the extent that we have no clear conception of it.

Without going into details about the determination of the reaction order, it may be pointed out that Figure 4 shows that in this case also, that is, for all initial concentrations of sulfur, the reaction order is 0.8; for, as can be plainly seen, straight lines are obtained by the suitable plotting of the experimental data.

It is important here to point out that the slope of the curves given in Figure 4 becomes smaller as the initial concentration of the sulfur is increased; thus the rate constant for the 0.8 order of sulfur decrease is not independent of the

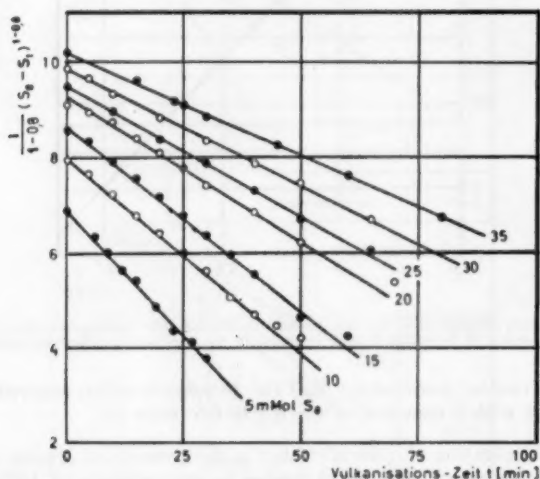


Fig. 4.—Decrease in sulfur concentration according to an 0.8 order reaction in the vulcanization at 130° C of Perbunan N 2818 with constant DPG content (10 m moles) and increasing sulfur concentration (5 to 35 m moles S_8) in 100 g of mixture. Ordinate: As given. Abscissa: Vulcanization time, t (min).

initial concentration of sulfur but actually becomes less with increasing concentration. This is a result which should not be expected if the decrease in sulfur is the result of a single reaction which satisfies the conditions used for the derivation of the time laws of chemical kinetics. If vulcanization as measured by the sulfur decrease were not a complex reaction, the rate constant for the sulfur decrease should be independent of the initial concentration. The fact that we are observing a dependence of the rate constant on the initial concentration points out that the dependence of the initial rate of sulfur decrease, $[d(S_8)/dt]_0$, on the initial concentration of sulfur will not follow the same law as is followed by the decrease of sulfur concentration with time ($n = 0.8$); and this expresses what was previously designated as the discrepancy in the reaction order when based on the reaction time and the concentration of reactant, that is, sulfur. This is no rarity in the kinetics of chemical reactions, but is an indication of the complex nature of the fundamental chemical mechanism.

Figure 5 shows that the rate constant of the sulfur decrease of order 0.8, corresponding to the falling off of the slopes of the curves of Figure 4, rises on a

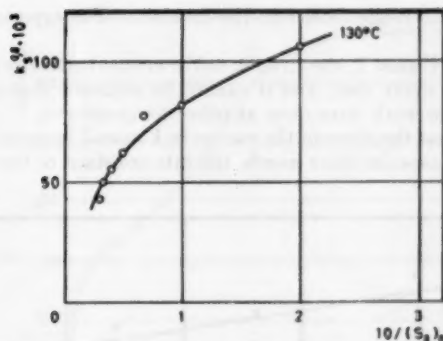


FIG. 5.—Dependence of the rate constant of the 0.8 order reaction for sulfur decrease shown in Figure 4, upon the reciprocal of the initial sulfur concentrations.

concave curve with increase in the reciprocal of the initial concentration of sulfur. Of yet greater importance for understanding the fundamentals is the plotting of the initial rate of sulfur decrease against the initial concentration, in keeping with previous considerations. Since the time law is known, ($n = 0.8$), according to which the free or unreacted sulfur changes, we can calculate the initial rate by substituting in Equation (1) the rate constants which have been found.

$$[d(S_8)/dt]_0 = k \cdot (S_8)_0^{0.8} \quad (1)$$

When the values obtained in this way are plotted against the initial concentration of sulfur, we get the curve of Figure 6. It has a different character from the curve of Figure 5; in the lower range of sulfur concentrations, it rises with a slight curvature, and then at higher concentrations bends over to become horizontal. Here the rate of sulfur decrease is practically independent of sulfur concentration and becomes constant. We may note that this result corresponds to relations which were observed with vulcanizations in the presence of constant sulfenamide content and with changing sulfur concentrations¹.

We may now examine the kinetics of sulfur decrease with varying DPG content. For this purpose the initial concentration of sulfur was kept constant at 10 mmoles of S_8 for 100 g of mixture, while the accelerator content was varied

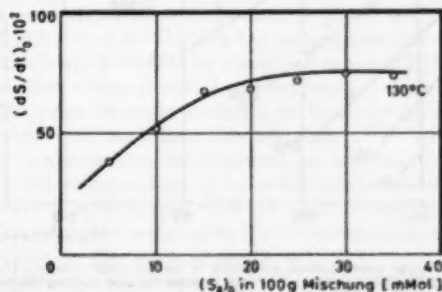


FIG. 6.—Dependence of the initial rate of sulfur decrease from Figure 4 upon the initial concentration of sulfur. Ordinate: As given. Abscissa: $(S_0)_0$ in 100 g of mixture (mmoles).

stepwise through the range from 1 to 150 mmoles. The experiments were run at 115° C.

As is shown in Figure 7, the drop in sulfur concentration here obeys a time law of order 0.8 in every case, and it cannot be assumed that there would be any difference if the work were done at other temperatures.

We now note that the slope of the curves in Figure 7 becomes greater as the DPG content increases; in other words, the rate constant of the reaction of 0.8

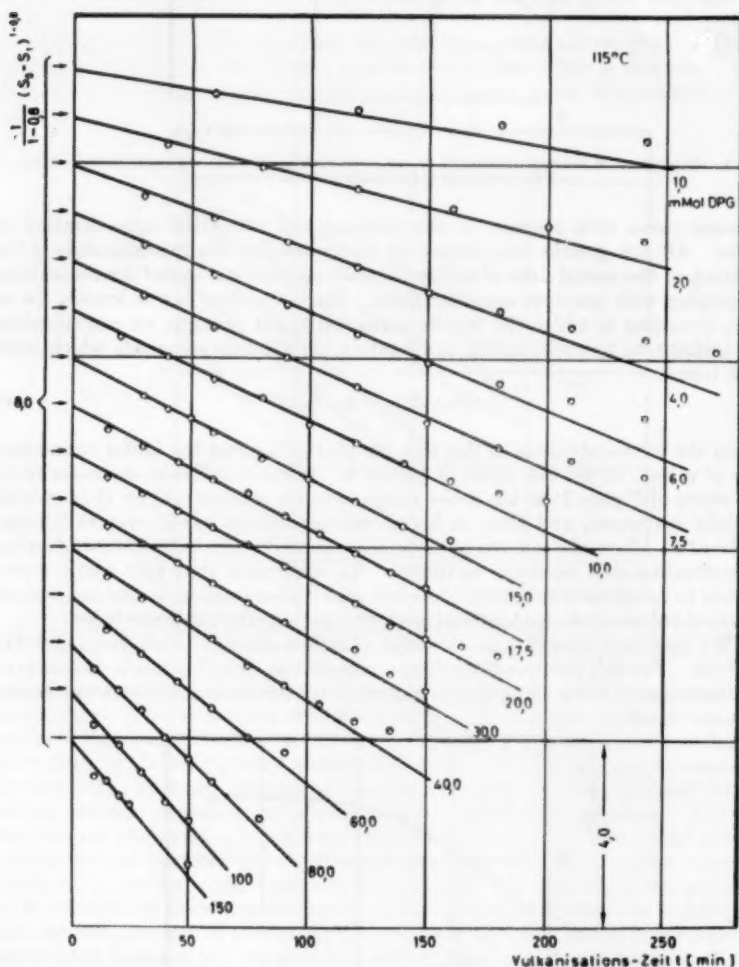


FIG. 7.—Decrease in sulfur concentration according to an 0.8 order reaction in the vulcanization at 115° C of Perbunan N 2818 with constant sulfur (10 mmoles S_0) and varying diphenylguanidine content (1 to 150 mmoles) in 100 g mixture. The curves are displaced along the ordinate each by a constant amount. The value of the function when $t=0$ in each case equals 8.0; the arrows indicate the start of the reaction. Ordinate: As given on the plot. Abscissa: vulcanization time, t (min).

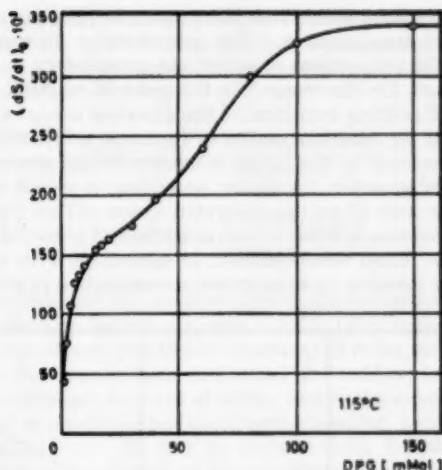


FIG. 8.—Dependence on the initial rate of sulfur decrease in Figure 7 upon the diphenylguanidine content. Coordinates: As given on the plot.

order increases, and therefore, since $(S_0)_0 = \text{const.}$, the initial rate of sulfur decrease must rise in the same way. Everything here is exactly opposite to what was found for the results plotted in Figure 4. But it is not surprising that the rate rises with increase in accelerator content; the main question is how the functional relationship between it and the initial concentration of DPG comes about. That is shown in Figure 8. We can see there how the initial rate of sulfur drop rises along a curve which has a point of inflection at about 25 mmoles of DPG, passes through an intermediate stage and above 100 mmoles becomes practically independent of accelerator concentration.

The course of the curve in Figure 8 agrees with our experience¹⁰ in that the rate of sulfur decrease does finally become constant. In our investigations with natural rubber, we have never yet found a curve with an inflection point which, after all, has the shape of an electrometric titration curve for a binary electrolyte, and gives the suggestion of the overlapping of two relationships as that given in Figure 6. Since the first important fall-off in the increase of rate occurs in practically the same concentration range as that found in Figure 6, namely between 20 and 25 mmoles of DPG, then the subsequent rise in the rate as well as its return to constancy indicated at about 100 mmoles DPG, may have their origin in some reaction which is not at present known.

The attempt may now be made to clarify particularly the course of the curve in Figure 6. To this end, we collect the following:

a) The sulfur concentration decreases at all temperatures according to a reactions of order 0.8, independent of its initial concentration and also of the DPG content; there is no evidence that the order of reaction varies with the temperature. Therefore the occurrence of a fractional order of reaction may be the result of catalysis by the reaction products¹¹.

b) The rate constant of the reaction of 0.8 order of sulfur decrease becomes smaller at constant DPG content with increasing initial sulfur concentration, while it becomes larger at constant sulfur concentration with higher DPG con-

tent. This state of affairs points to a discrepancy in the order of reaction with respect to time and concentration. The rate of sulfur decrease is therefore a function of the molar proportions of sulfur and accelerator.

c) In our opinion, the discrepancy in the order of reaction would probably be observed even if nothing complicated the situation except an autocatalysis, that is, a catalysis by reaction products (perhaps polysulfide crosslinking). But then the dependence of the initial rate upon initial concentration should follow a whole number order. Actually, according to recent work by Scheele and Echte¹², in the case of an unaccelerated (pure sulfur) vulcanization, the sulfur decrease in relation to time follows a reaction of order 0.6 (autocatalysis) but with respect to initial concentration, in agreement with van Rossem¹³, it follows a first order reaction up to an initial concentration of about 20% sulfur.

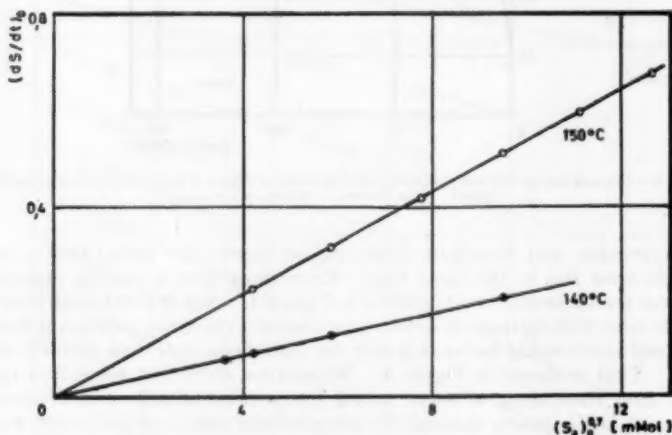


Fig. 9.—Dependence of the initial rate of sulfur decrease as a 0.7 order process, upon the initial concentration in the vulcanization of natural rubber in the presence of the zinc salt of mercaptobenzothiazole, according to Scheele and Echte.

d) In accelerated vulcanizations however, the dependence of the initial rate upon initial concentration generally does not follow a whole number order. Agreement among orders with respect to time and concentration was found only in vulcanizations with MBT as accelerator in the presence of zinc oxide, in studies made by Echte and Scheele¹⁴. This is seen in Figure 9, which shows that straight lines are obtained at 140° and 150° C, when the initial rates of sulfur decrease calculated from the rate constants of 0.7 order are plotted against the 0.7 power of the initial concentrations. However, it is generally found that the initial rate at first rises when the accelerator content is constant and the sulfur concentration is rising as well as when the sulfur is constant and the accelerator content is varied, but finally becomes independent of both of the reactants.

The very fact that in the great majority of accelerated vulcanizations, it is impossible to define the correlation between initial rate and concentration of reactants by means of a law with an integral exponent, leads us to try to associate the previously found kinetic relation with the appearance of intermediate compounds¹⁵; and it is the characteristic course of the curves in Figures 6 and 8 which induces us to use such a view point to explain what has been found.

Leaning on relevant statements by Laidler¹⁶ and others², we have earlier come to the opinion that the rate of sulfur decrease accompanied by the formation of an intermediate compound from the accelerator and sulfur, should conform to some such law as the following:

$$[d(S_8)/dt]_0 = \frac{k(S_8)_0(B)_0(Ka)}{(S_8)_0 + 1/K} \quad (2)$$

$$[d(S_8)/dt]_0 = \frac{k(S_8)_0(B)_0(Ka)}{(B)_0 + 1/K} \quad (3)$$

In these equations $(S_8)_0$ and $(B)_0$ represent the initial concentrations respectively of sulfur and accelerator (in our example, DPG); (Ka) is the concentration of rubber (since it is in excess, practically constant); k is the rate constant for the reaction between the intermediate compound and rubber, and, hence the rate constant for concentration decrease of sulfur, and K the constant of a proposed equilibrium which is quickly established between sulfur, accelerator and intermediate reaction product. It may be derived from Equations (2) and (3) that the intermediate compound of the equilibrium mentioned (possibly an amine polysulfide) reacts with rubber more slowly than the proposed equilibrium becomes established. Finally, it must be mentioned that the equations describe the relationships for final excess of sulfur Equation (2), and accelerator, Equation (3).

When the initial concentration of sulfur or of accelerator (DPG) in Equations (2) and (3) is very much smaller than $1/K$, which will be the case especially when K itself and also $(S_8)_0$ and $(B)_0$ are small, then the rate of sulfur decrease will rise in both cases with the sulfur concentration or the DPG content. But if $(S_8)_0$ and $(B)_0$ are large and greater than $1/K$, which will be true when K itself is large, then the rate of sulfur decrease must eventually become constant, because $1/K$ in the denominator of Equation (2) and Equation (3) becomes of less and less effect and may finally be disregarded. Thus, in the one case the initial rate becomes independent of sulfur concentration at constant DPG content, and in the other case it becomes independent of accelerator content at constant sulfur concentration. However, there will be transition stages between these two limiting cases. At what reactant concentrations the one or the other will be observed should depend largely upon the equilibrium constant K , but at present we have no numerical values for this.

It can be seen that the experimental results which are shown in Figures 6 and 8 are at least fundamentally in agreement with Equations (2) and (3). In our opinion, however, this does not mean full certainty of the correctness of the views which have been developed. To attain complete clarity in the matter we would have to gain more knowledge about the proposed equilibrium as well as about the structure and constitution of the intermediate product. We are still far short of this.

In this connection, it should be made clear that a certain portion of the DPG which is introduced is always used up in the vulcanization, that is, it cannot be recovered. Cherubim¹⁷ has previously called attention to this and has noted this same thing in cases of acceleration by other bases.

We show these relations in Figure 10 for the previously mentioned case of Perbunan N 2818 accelerated by DPG and vulcanized at 115° C. The portions of the DPG still present after 200 minutes of reaction time, as found in the

extracts of the vulcanizates, are plotted as mmoles (ordinate) against its initial concentration in mmoles (upper curve). The initial concentration of the sulfur was 10 mmoles in every case. The difference between the amount of DPG which was introduced and that which was recovered, gives the portion of the DPG in mmoles which was consumed (lower curve).

It can be seen that the millimolar consumption of accelerator rises until the initial content in the rubber mixture reaches 100 mmoles, yet the percentage consumption of the DPG is practically constant at about 22.5 per cent of the amount introduced at each point. Now since the maximum millimolar consumption of DPG is about double the initial sulfur concentration, so that for every molecule of S_8 , about two molecules of DPG are converted, and this maximum consumption takes place only at large excess of DPG, we may conclude that we are not dealing here with the formation of just one intermediate com-

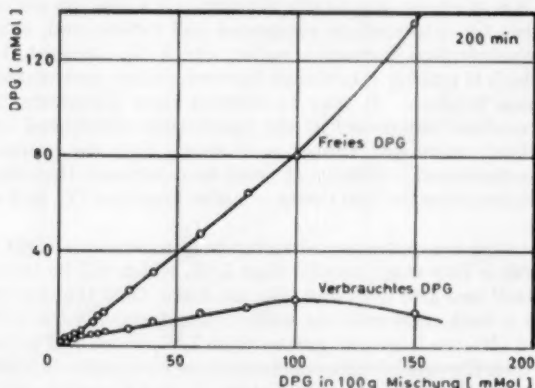


FIG. 10.—Relationship between consumed and recovered diphenylguanidine and its initial content in the vulcanization of Perbunan N 2818 at 115°C ($(S_8)_0 = \text{const.}$). Ordinate: As given. Abscissa: DPG in 100 g mixture (mmoles). On curves: Freies DPG: Unreacted DPG. Verbrauchtes DPG: Consumed DPG.

pound. If the latter were not the case, that is, if a single well-defined intermediate were being formed, then, since $(S_8)_0 = \text{const.}$, it is our opinion that the millimolar and not the percentage consumption of accelerator should be practically constant.

Actually, we could draw still other conclusions based on the relationships shown in Figure 10 if it were not for the fact that we have found that when Perbunan, which has been exhaustively extracted with methanol, is heated to higher temperatures with DPG (and in complete absence of any other added materials), a regular increase in the consumption of the base with reaction time is noted and although the reaction is slower than it is when sulfur is present (a relatively rapid disappearance of DPG is noted in the presence of sulfur), yet the relationships shown by Figure 10 may not be sufficiently exact. There is always the possibility, we believe, that the disappearance of DPG may indicate the formation of several similar intermediate compounds which may differ in composition only in the amount of sulfur which each contains. In our opinion, that would not alter the fundamental character of the considerations advanced previously, and the curves given in Figure 6 and 8 should be expected

to take the courses shown there, only the course would be the results of the superposition of several relationships which are to be described by Equations (2) and (3).

SUMMARY

In connection with earlier research work, we have carefully studied the decrease of sulfur during the vulcanization of Perbunan N 2818 in the presence of DPG, at various temperatures and with varied molar concentrations of sulfur and accelerator. We found:

1. The sulfur concentration decreases at all temperatures according to a time law of order 0.8. An activation energy of about 28 kcal/mole is derived from the temperature dependence of the rate constant.

2. The reaction order is independent of the initial concentration of reactants.

3. A discrepancy is found in the order of the reaction with respect to time and with respect to concentration, and it is clearly shown that the dependence of the initial rate on the initial concentration can not be expressed by a single power law.

4. The attempt is made to explain the discrepancy by postulating catalysis by an intermediate compound. The consequences from this consideration are compared with the experimental results, and, on the whole, agreement is found between theory and experiment.

REFERENCES

- ¹ Scheele, W., Toussaint, H. E., and Yuan-Kun Chai, *Kautschuk u. Gummi* **12**, WT 122 (1959).
- ² Scheele, W., and Cherubim, M., *Kautschuk u. Gummi* **10**, WT 185 (1957); also *Verhandlungsber. Kolloid-Ges.* **18**, 142 (1958).
- ³ Scheele, W., *Rev. gen. caoutchouc* **36**, 1695 (1959).
- ⁴ Lorenz, O., and Echte, E., *Kautschuk u. Gummi* **10**, WT 273 (1957); also Lorenz, O., *Verhandlungsber. Kolloid-Ges.* **18**, 142 (1958).
- ⁵ Scheele, W., Toussaint, H. E., and Yuan-Kun Chai, *Kautschuk u. Gummi* **12**, WT 122 (1959); also Skrabal, A., "Homogenkinetik", Dresden and Leipzig, 1941, p. 60.
- ⁶ Scheele, W., and Schaper, H., Unpublished research.
- ⁷ Scheele, W., and Müller, K. H., also Scheele, W. and Stemmer, H. D., Unpublished research.
- ⁸ In earlier investigations by Lorenz and Echte (*Kautschuk u. Gummi* **10**, WT 23 and 81 (1957)) the sulfur decrease in a vulcanization accelerated by mercaptobenzoethiazole in the presence of zinc oxide was found to follow a first order reaction. In the meantime, however, we have found that in this case too the process is more accurately described as a reaction of a fractional order.
- ⁹ Lorenz, O., and Echte, E., *Kautschuk u. Gummi* **10**, WT 273 (1957).
- ¹⁰ Scheele, W., and Cherubim, M., Reference 2, and Scheele, W., Reference 3; other examples are given there for a similar shape of curve.
- ¹¹ Reference should be made to van Iterson, Jr., G. (*Kunststoffe* **10**, 133, 152 and 169 (1917)) concerning an autocatalytic decrease of sulfur concentration during vulcanization.
- ¹² Scheele, W., and Echte, E., Unpublished research.
- ¹³ van Rossem, A., Comm. Netherlands Gov't. Advising Rubber Trade, Delft (1917).
- ¹⁴ Echte, E., and Scheele, W., Unpublished research.
- ¹⁵ Intermediate compounds are also assumed by other authors; for example, Moore, C. G., and Saville, R. W., *J. Chem. Soc. (London)*, 2082 and 2089 (1954). Also Krebs, H., *Gummi u. Asbest* **8**, 68 (1955) and *Angew. Chem.* **65**, 74 (1953). Blokh, G. A., *Рубер Снем. & Технол.* **31**, 1049 (1958) makes comment on the intermediate compound formed from DPG and sulfur.
- ¹⁶ Laidler, K. L., "Chemical Kinetics," McGraw-Hill Co., New York, 1950, p. 274.
- ¹⁷ Cherubim, M., Dissertation, Hannover (1957).

VULCANIZATION OF ELASTOMERS. 25¹. NATURAL RUBBER AND SYNTHETIC ELASTOMERS WITH SULFUR AND SULFENAMIDES. I *

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INTRODUCTION

Certain sulfenamides, such as N-cyclohexyl-2-benzothiazolylsulfenamide (CZ) are well known and used as accelerators for sulfur vulcanization; they also bring about a delayed crosslinking reaction, which makes processing safer². The mechanism of the vulcanization reaction has been treated by Dogadkin and coworkers³ in great detail; Fromandi and Reissinger² have agreed with them on the main points. Starting with the observation that SBR (Buna S) can be vulcanized with large amounts of sulfenamides, they postulate a decomposition of a sulfenamide $R_1-S-S-NH-R_2$ or $R_1-S-N(R_2)_2$ into radical fragments $R_1-S\cdot$ and $R_2-NH\cdot$, or $RS\cdot$ and $(R_2)_2=N\cdot$, respectively, which can react with the α -methylene groups as well as the double bonds of the allylic units to form a corresponding polymer radical. This can in turn undergo various transformations that lead to crosslinking; a linear relationship between strain values and the sulfenamide bound by the polymer exists. The investigators concluded that reactions of this type also play an important part in a sulfenamide accelerated sulfur vulcanization; Fromandi and Reissinger see a certain analogy between thiuram disulfides and sulfenamides in regard to their behavior during vulcanization. Actually, Craig and coworkers⁴ were able to show that thiuram disulfide when present in large enough amounts can cause a certain amount of crosslinking in rubber even in the absence of zinc oxide.

It is also known that a sulfur vulcanization accelerated with a mixture of mercaptobenzothiazole (MBT) and cyclohexylamine proceeds faster than in the presence of only one of these additives; according to Fromandi and Reissinger², the rate of vulcanization is highest when MBT and bases are present in equimolar quantities. If one considers that large amounts of MBT are formed during a sulfur vulcanization accelerated with the corresponding sulfenamide, the question arises whether vulcanization in the presence of sulfenamides may in principle be identical with one using the corresponding ammonium salt if one can disregard the induction period observed when sulfenamides are used. Obviously, the question can be decided best by accurate kinetic measurements of the decrease in sulfur concentration during vulcanization. The present work should contribute to the elucidation of this problem; results also point to the complications encountered in the interpretation of the kinetics of sulfur vulcanization.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by O. C. Elmer from *Kautschuk und Gummi*, Vol. 12, Pages WT 122 to 128, May 1959. Tables of data have been omitted to save space.

EXPERIMENTAL PROCEDURES

All experiments were made with Perbunan N 2818 (butadiene-acrylonitrile copolymer). The crude rubber was exhaustively extracted in a Soxhlet apparatus with methanol, to remove inhibitors as well as impurities introduced during polymerization. The rubber was cut into small pieces and air dried; it was then sheeted out on a rubber mill. Sulfur was added first and the sulfenamide second; the mixture was "homogenized" (mixed) on a tight mill with good cooling. Vulcanizates were prepared in the usual manner. Their color changed from light brown to dark brown after a short vulcanization interval, to black after longer reaction periods; no doubt among other things the color is due to the formation of polysulfide bonds. The sulfenamide used was CZ. Since the technical product contained impurities and was difficult to purify by recrystallization, it was decided to prepare it from mercaptobenzothiazole (MBT) and cyclohexylamine. The following general procedure was followed⁵: a suspension of MBT and cyclohexylamine was prepared in aqueous alcohol and portions of sodium hypochlorite added with agitation. CZ which precipitated as colorless needles as the NaOCl was added was filtered off, and washed with water until free of chloride ions. The needles melted at 99–100°. Pure CZ thermally was quite stable. After three hours of heating to 140° no change in melting point had occurred. It was less stable in solution, particularly in the presence of impurities. However, acetone solution of the analytically pure material showed no change after several days.

CZ reacts with sulfur to give cyclohexylamine and hydrogen sulfide; when this reaction takes place in boiling xylene, the cyclohexylammonium salt of MBT is formed; this same salt is also formed on heating benzothiazolyl disulfide with cyclohexylamine in xylene. From this reaction it may be expected that the cyclohexylammonium salt of MBT would also form during vulcanization, and it would be necessary to determine it in the presence of the sulfenamide. Since no direct titrimetric method for the determination of CZ could be found, one had to be satisfied with an indirect method. A procedure follows: an acetone solution containing CZ as well as cyclohexylammonium salt of MBT is diluted with water in a conductivity cell. After addition of 0.1 ml (0.1 molar) cyclohexylamine, the solution is titrated with a standard solution of silver nitrate⁶; the amount of MBT present in salt form is titrated in this procedure. A 10 ml portion of a 5% solution of SnCl_2 in 20% hydrochloric acid is added to another part of the solution to be tested and heated under reflux for 25 minutes. This leads to the reduction of CZ and formation of the respective ammonium salt. After the reaction is finished, the acetone is removed under vacuum, the residue is diluted with water and the MBT is repeatedly shaken out with ethyl acetate. The combined ethyl acetate extracts are evaporated on the steam bath, taken up in acetone, diluted with water and titrated conductimetrically with standard silver nitrate solution; thereby the total content of MBT present as salt and as sulfenamide is determined. The difference of the two titrations gives the content of sulfenamide.

The free sulfur in the vulcanizate extract was determined by the somewhat modified procedure⁸ of W. Scheele and Chr. Ilschner-Gensch⁷. Sulfur reacts with KCN to give KSCN, and after removal of excess KCN with 98% formic acid (evaporating and drying in vacuum and dissolving the residue in water) it is titrated conductimetrically with silver nitrate after the interfering MBT had been extracted with ethyl acetate.

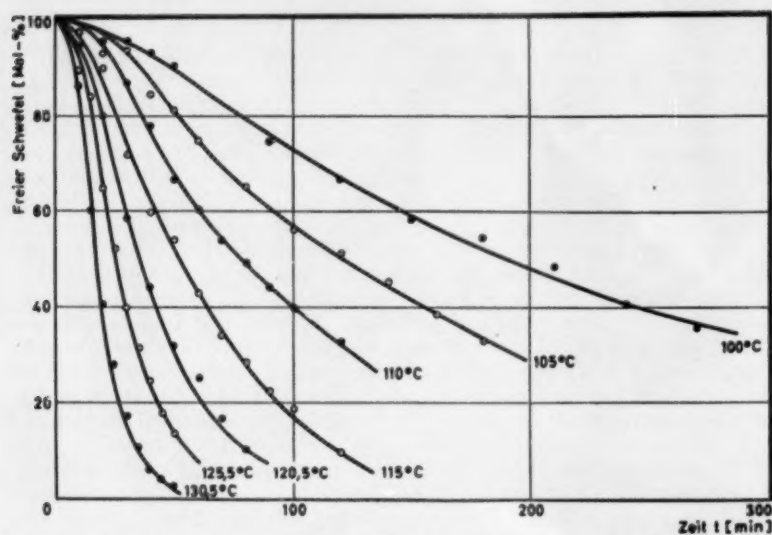


FIG. 1.—Decrease of sulfur concentration at different temperatures during vulcanization of Perbunan N 2818 with sulfur (10 mmoles S₈) in the presence of CZ (10 mmoles in 100 g compound). Ordinate: Free sulfur (mole-%). Abscissa: Time t (min).

RESULTS AND DISCUSSION

At first we investigated the decrease in sulfur concentration during vulcanization as function of temperature. Each 100 g of Perbunan compound contained 2.56 g S (10 mmoles S₈) and 2.64 g CZ (10 mmoles). Table I (omitted from this translation) gives the free sulfur content in mole% of vulcanizates at

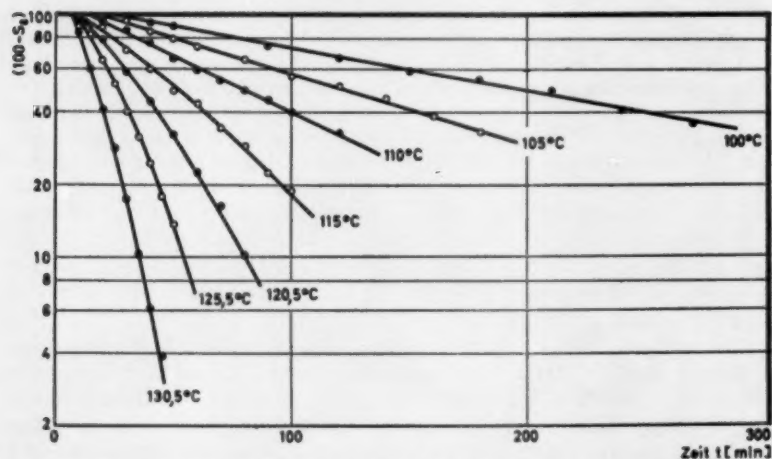


FIG. 2.—Decrease of sulfur concentration according to Table I and Fig. 1 plotted according to 1st order. Abscissa: Time t (min).

different vulcanization times and temperatures; Figure 1 shows these results graphically. The curves were drawn to intersect the ordinate at 100% starting concentration; this makes it possible to recognize a slower initial reaction period. After passing a turning point, which coincides approximately with the so-called scorch or induction period the curves show a gradual decrease in reaction rate.

Figure 2 shows an attempt to plot the results according to first order kinetics. It appears that the decrease in sulfur concentration approximates the 1st order law throughout a large portion of the curves, particularly in the case of the 100°, 195°, and 110° plot; in the case of higher temperatures that also cover higher conversions, straight lines are no longer obtained. From the curvature (concave) of the lines one must conclude that the reaction order is less than one. Figure 2 also makes the scorch period apparent, which extends at lower tem-

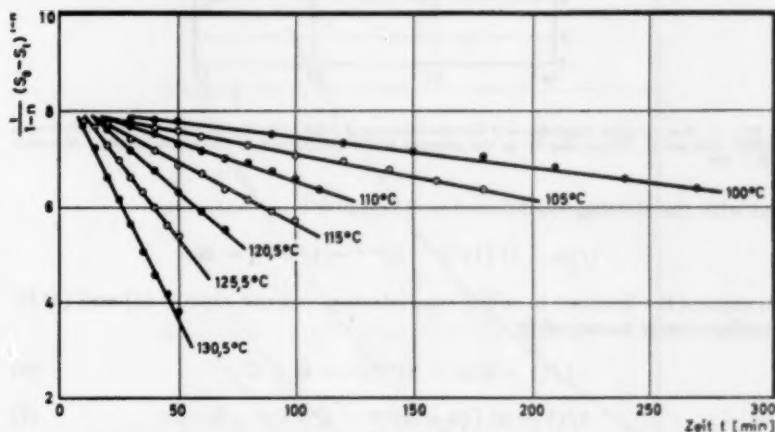


FIG. 3.—Decrease of sulfur concentration according to Table I and Fig. 1 plotted to the 0.8th order. Abscissa: Time t (min).

perature through a longer span. We determined the reaction order graphically. For a reaction of any order the following holds (a = starting concentration of reactants and x = amount reacted)

$$dx/dt = k(a - x)^n \quad (1)$$

$$\text{and} \quad \log dx/dt = \log k + n \log (a - x) \quad (2)$$

$$\text{or} \quad \log \Delta x/\Delta t = \log k + n \log (a - x) \quad (3)$$

If one plots therefore $\log \Delta x/\Delta t$ against $\log (a - x)$ one obtains in the case of a continuous reaction of the n -th order, within the accuracy determined by unavoidable analytical errors, straight lines with the slope n . By this method a reaction order $n = 0.8$ was found by averaging all cases investigated. One can test the value of n by suitably plotting experimental results. Integration of (1) gives

$$1/(n - 1) 1/(a - x)^{n-1} = kt + C \quad (4)$$

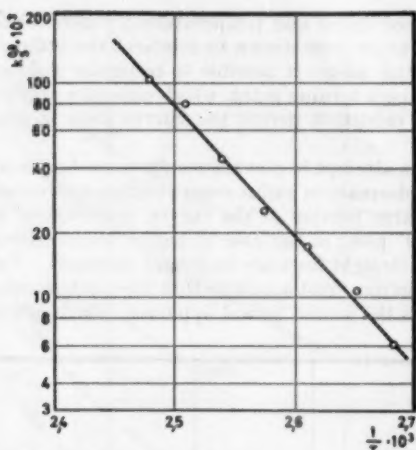


FIG. 4.—Temperature dependence of the rate constant of 0.8th order during vulcanisation of Perbunan N 2818 with sulfur (10 mmoles S_8) in the presence of CZ (10 μ moles in 100 g compound). Abscissa: $1/T \cdot 10^3$.

and with the starting conditions $t = 0$ and $x = 0$

$$1/(n-1) [1/(a-x)^{n-1} - 1/a^{n-1}] = kt$$

To express the decrease in sulfur concentration one can express (4) and (5) by simultaneously transposing

$$1/(1-n)(a-x)^{1-n} = -kt + C \quad (6)$$

and

$$1/(1-n) [(a-x)^{1-n} - a^{1-n}] = -kt \quad (7)$$

We proceed then to investigate what happens when an equivalent of cyclohexylammonium MBT salt instead of CZ was added directly to Perbunan. There-

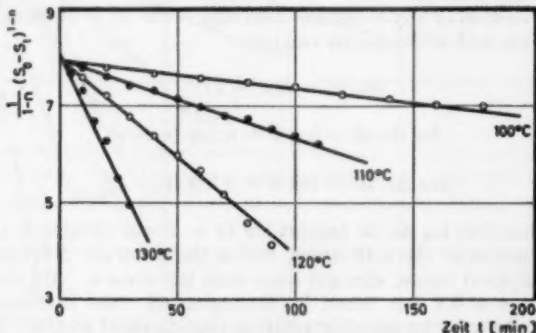


FIG. 5.—Decrease of sulfur concentration at different temperatures according to 0.8th order during vulcanisation of Perbunan N 2818 with sulfur (10 mmoles S_8) in the presence of cyclohexylammonium benzothiasoyl mercaptide (10 mmoles in 100 g compound). Abscissa: Time t (min).

fore, we add to 100 g rubber compound 2.56 g S (10 mmole S_0) and 2.66 g (10 mmole) of the cyclohexylammonium salt of MBT. We investigated only four temperatures. The results are listed in Table II (omitted from this translation). Figure 5 shows that under the present conditions an 0.8th reaction order also applies; for one obtains straight lines when plotting $1/1-0.8(a-x)^{1-0.8}$, that is $1/1-0.8(S_0-S_t)^{1-0.8}$ against the vulcanization time ($S_0 = S_0$

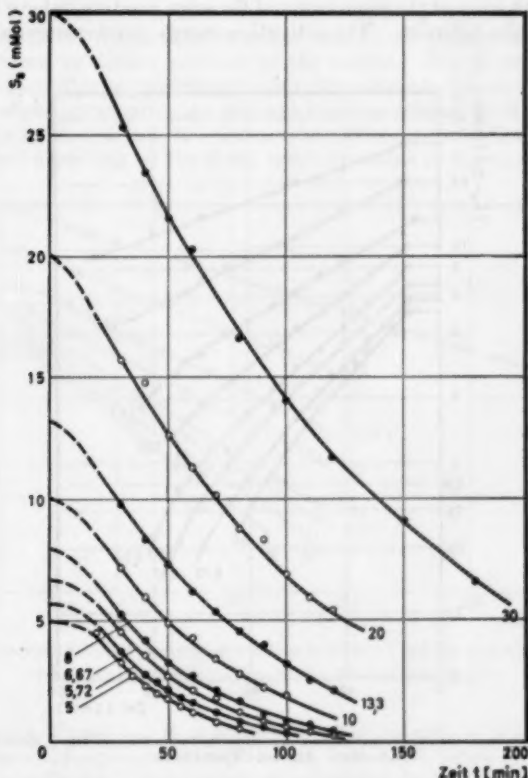


FIG. 6.—Decrease of sulfur concentration at different starting concentrations (5.0...20 mmole S_0) and constant CZ content (10 mmole in each 100 g compound) at 115°. Ordinate: S_t (mmole). Abcissa: Time t (min).

concentration at the beginning, $S_t = \text{bound } S_0$). It becomes apparent that the induction period is no longer observed. The assumption is therefore attractive that the "initiation" period clearly seen in Figure 3 is due to the ammonium salt building up at the start of the reaction.

The rate constants of 0.8th order calculated from the slopes of the curves in Figure 5 are also listed in Table II. Comparing those with the constants of Table I, good agreement is found between the values, i.e., the decrease in S concentration during vulcanization in the presence of CZ proceeds at roughly the same rate as in the presence of cyclohexylammonium MBT salt. The only

difference between the two vulcanizations seem to be the scorch or induction period found only with CZ. We are therefore of the opinion that the kinetics of sulfur disappearance are neither decided nor dominated by the initially mentioned radical reaction formulated by Dogadkin and coworkers; the plausible radicals made responsible by these workers for the vulcanization of Buna-N (nitrile rubber) with sulfenamide could not form from the ammonium salt of MBT. It would be implausible that the decrease in sulfur concentration would proceed in both cases at the same rate and the same reaction order if the reaction mechanisms were different. The activation energy, furthermore, was the same in both cases.

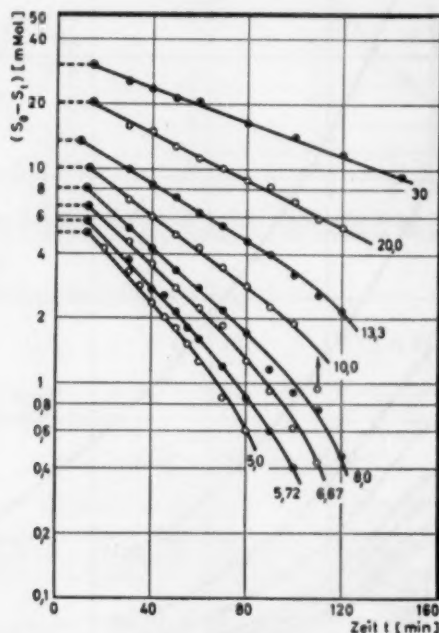


FIG. 7.—Decrease of sulfur concentration according to Table III and Fig. 6 plotted to the 1st order. Abscissa: Time t (min).

It is clear that a complex process must be behind the fractional order of sulfur concentration decrease. We think that when we measure the decreasing sulfur concentrations we are actually following in the present case the decomposition of a reactive intermediate. Sulfur vulcanizations accelerated with DPG or MBT may be similar type reactions. We therefore investigated the kinetics of sulfur concentration decrease at different sulfur starting concentrations and constant CZ content and also at variable CZ starting concentrations with constant sulfur concentration.

First, we will consider the case of variable sulfur starting concentrations. These experiments were conducted at 115° . The CZ content again was 2.64 g (10 mmol) in 100 g Perbunan compound. The sulfur concentration was varied between 5 and 30 mmol S_0 , respectively 1.28 and 7.68 g S in 100 g

compound. The results are listed in Table III (omitted from this translation), where sulfur disappearance is expressed in terms of per cent as well as mmoles S_8 with the vulcanization time. Because of our concern to describe the kinetics of decreasing sulfur concentration as accurately as possible, we show in Figure 6 the decreasing sulfur concentrations plotted against the vulcanization time at 115° and the starting concentrations given in Table III. The general shapes of the curves are similar to those in Figure 1; but one notices that the rate of disappearance of sulfur clearly increases with increasing starting concentration and the question of reaction order arises again. An induction period is observed expressed as dashed portions of the curves. If one plots the experimental data according to the first order law, the curves in Figure 7 are obtained. They show slight curvature. An average reaction rate order of 0.8 was again found. As a matter of fact, the decrease in sulfur concentration can again be well described according to the 0.8th order law; this is shown clearly by the

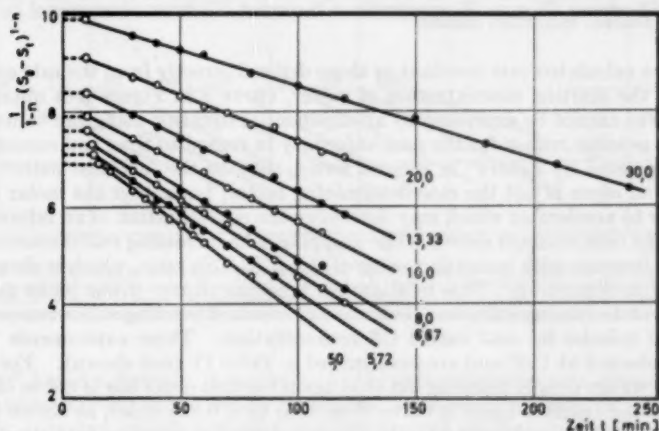


FIG. 8.—Decrease of sulfur concentration according to Table III and Fig. 6 plotted to the 0.8th order. Ordinate: $\frac{1}{1-n} (S_0 - S_t)^{1-n}$. Abscissa: Time t (min).

straight lines in Figure 8. It is noteworthy that in spite of the fact that the $CZ:S_8$ changes throughout the experiment, one single value for the reaction order (0.8) is sufficient. Rate constants calculated from the slope of the lines in Figure 8 are also included in Table III.

Normally, it is expected that the rate constant of any reaction of the n th order should be independent of the starting concentration of the reactants. However, the curves in Figure 8 and numerical values in Table III show that the rate constants in this case depend on the beginning concentration of sulfur as had been found in the MBT accelerated sulfur vulcanization⁹; their value decreases with increasing sulfur concentration. It should therefore not be expected that the starting rate of reaction $(d(S_0)/dt)_0$ and the starting sulfur concentration be related according to an equation containing 0.8 as exponent. If one plots the value for $(d(S_0)/dt)_0$ as calculated from equation

$$(d(S_0)/dt)_0 = k (S_0)^{0.8} \quad (10)$$

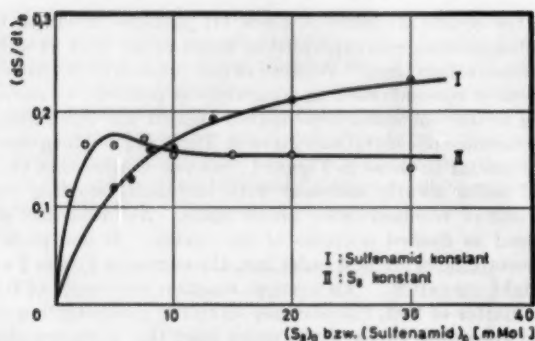


Fig. 9.—Dependence of starting rate of decreasing sulfur concentration on starting concentration of sulfur at CZ-constant (I), or on CZ concentration at S_8 -constant (II) during vulcanisation of Perbunan N 2818. Abscissa: $(S_8)_0$, $(CZ)_0$ (mmole).

using the calculated rate constant or those derived directly from the rate curves against the starting concentration of sulfur, curve I in Figure 9 is obtained. This curve cannot be expressed by an exponential equation using the value 0.8.

The possible reason for the nonconformity in regard to time and concentration, discussed by Letort¹⁰ in general terms, may be the fact that sulfur concentration alone is not the rate determining factor, but rather the molar ratio of sulfur to accelerator which may determine the concentration of an intermediate. The rate constant shows, while dropping with increasing sulfur concentration, an increase with increasing value of the $(CZ)/(S_8)$ ratio, which is shown in Curve I in Figure 10. This relationship becomes clearer if one looks at the kinetics of decreasing sulfur concentration at constant starting sulfur concentration (10 mmole S_8) and varied CZ concentration. These experiments were also conducted at 115° and are summarized in Table IV (not shown). For lack of space we are simply pointing out that again the first order law is not in effect, but that the reaction again is better described by a 0.8th order, as shown from the straight lines in Figure 11. If one calculates the reaction rate constants (Table IV) from the slopes in Figure 11 and plots those values against the molar

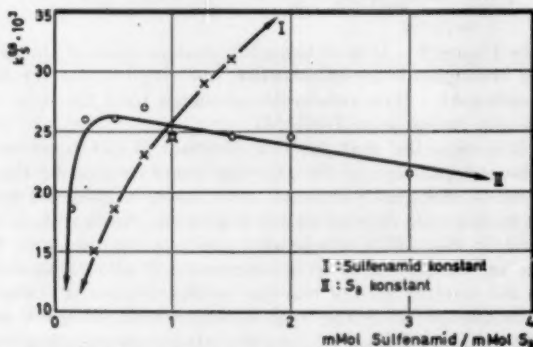


Fig. 10.—Dependence of the 0.8th order rate constant of the decreasing sulfur concentration on the molar ratio $CZ:S_8$ during vulcanisation of Perbunan N 2818. (I) CZ-constant, (II) S_8 -constant. Abscissa: mmole CZ/mmole S_8 .

ratio (CZ)/(S₀), Curve II in Figure 10 is obtained, which is quite different from Curve I. A similar result is obtained if one calculates starting rate of decreasing sulfur concentration by Equation (10) by using the rate constants of Table IV and plots these values against starting concentrations of CZ, shown by Curve II in Figure 9. It should be mentioned that a number of curves exist that follow the general shape of II in Figures 9 and 10 if one measures the starting rate, or rate constant at different, but for each case constant starting concentration of sulfur in relation to the CZ concentration.

The kinetic relationships found give an indication of the extreme complexity of the accelerated sulfur vulcanization. However, similar conditions were found in investigations of sulfur vulcanization accelerated with ZnO¹¹ and diphenylguanidine¹²; a number of technical vulcanizations have therefore certain kinetic characteristics in common. Even when sulfur disappearance is interpreted as a 1st order process, which may be an approximation, Lorens and

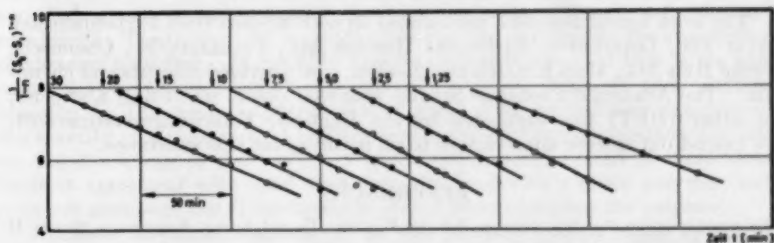


FIG. 11.—Decrease in sulfur concentration at 115° and varying starting content of CZ, but constant sulfur concentration (10 mmoles S₀ in 100 g of compound) plotted to the 0.8th order during vulcanization of Perbunan N 2818. Curves are displaced along the abscissa, arrows indicate the start of the reaction, numbers next to arrows give the CZ concentration in mmoles (in 100 g of compound). Abscissa: Time *t* (min).

Echte¹¹ found a decrease in the value of the sulfur-decrease rate constant with increasing starting sulfur concentration and constant MBT content. In other words, they had already noticed the discrepancy in reaction rate with regard to time and concentration, that one would like to relate to the presence of an intermediate which would be the actual vulcanizing agent. Some indication of the formation of such compounds of increased reactivity was obtained from the results obtained in DPG accelerated vulcanization; one can only speculate as to the nature of such compounds and their concentration in rubber. The decreasing sulfur concentration followed a 0.7th order in that case; however, the rate constants increased with increasing DPG concentration (S₀ = constant), which indicates that the kinetics are controlled by an intermediate, and that the process should be viewed on that basis^{12, 13}.

SUMMARY

The sulfur vulcanization of Perbunan N 2818 (acrylonitrile-butadiene) was investigated in the presence of N-cyclohexyl-2-benzothiazolylsulfenamide (CZ) at different temperatures and various concentrations of reactants. The following were found:

1. The decreasing sulfur concentration vs. time plot followed the 0.8th order under all experimental conditions and an activation energy of 28.2 kcal/mole was calculated.

2. When using the cyclohexylammonium salt of MBT as accelerator, sulfur decrease proceeds at the same rate as with CZ.

3. It was concluded from 1 and 2 that even in the presence of CZ, the ammonium salt was the actual accelerator, which forms during the scorch or induction period through reaction of CZ with the rubber.

4. In view of the discrepancy found in the relation of reaction order with respect to time and concentration of reactants, the formation of a reactive intermediate is postulated; the analogy between the kinetics of sulfenamide accelerated sulfur vulcanization, and those accelerated with MBT as well as DPG is pointed out.

5. In connection with 3 the dependence of starting rate as well as rate constant of 0.8th order of the decreasing sulfur concentration on the molar ratio of CZ/S₈ and on the sulfur starting concentration is discussed.

ACKNOWLEDGMENT

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REFERENCES

- ¹ For communication 24 in this series see Scheele, W., Mau, G. and Keeme, *Kautschuk u. Gummi* 12 WT 33 (1959).
- ² Fromandl, G. and Reissinger, S., *Kautschuk u. Gummi* 11 WT 3 (1958).
- ³ Dogadkin, B. A., Feldstein, M. and Pevsner, B., *RUBBER CHEM. & TECHNOLOGY* 29, 933 (1956).
- ⁴ Craig, D., Juve, A. E. and Davidson, W. L., *J. Polymer Sci.* 5, 713 (1950).
- ⁵ Compare B.P. 655,668 (1951).
- ⁶ Compare also Lorenz, O. and Echte, E., *Kautschuk u. Gummi* 9, 300 (1956).
- ⁷ Scheele, W. and Hiescher-Gensch, Chr., *Kautschuk u. Gummi* 8, 55 (1955).
- ⁸ Birghan, Kl., Dissertation Hannover (1959), Cherubim, M., Dissertation Hannover (1957).
- ⁹ Lorenz, O. and Echte, E., *Kautschuk u. Gummi* 10, 273 (1957).
- ¹⁰ Letort, M., *J. chim. phys.* 34, 206 (1937), and *Bull. Soc. chim. France* 9, 1 (1942); also Laidler, K. J., "Chemical Kinetics" (New York and London, 1950) p. 17.
- ¹¹ Lorenz, O. and Echte, E., *Kautschuk u. Gummi* 10, 23 (1957), also 10, WT 81 and 273 (1957).
- ¹² Scheele, W. and Cherubim, M., *Kautschuk u. Gummi* 10, WT 185 (1957); Report of the Kolloid-Gesellschaft 18, 115 (1958).
- ¹³ Laidler, K. J., Reference 10.

THE ROLE OF HYSTERESIS IN TIRE WEAR AND LABORATORY ABRASION *

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INTRODUCTION

The power of abrasion experiments to predict wear of tires is limited. Correlation between laboratory and road is contingent upon close adherence to specified severities and generally breaks down when different polymers are compared. The influence of severity of service can be traced to the appearance of abrasion patterns¹. It has been suggested² that the wear of tires is the outcome of two processes, called respectively "intrinsic abrasion" and "pattern abrasion." The relative contribution of these wear mechanisms depends on the severity of service so that relative ranking of any two compounds depends on the conditions of the test^{3,4}. A quantitative development of these ideas leads to agreement with road wear data obtained with a given polymer, but does not surmount the difficulty encountered when changing the polymer.

Abrasion machines common in the tire industry employ small solid test wheels running with slip against an abrasive. Results of such measurements, apart from disagreeing with road data, often bear no relation to results obtained in simple sliding experiments. These observations suggest that the wear process of slipping wheels and tires depends not only on abrasion resistance, but also on other properties of the wheel. An investigation in these factors⁵ shows that the elastic constants play an important role in the wear of slipping wheels. The present paper gives an account of the theory and of its experimental verification.

SLIDING OF SLIPPING WHEELS

Slip velocity is defined as vectorial difference between traveling and circumferential velocities in the area of contact, all velocities being referred to the axle of the wheel. To maintain slip, a system of forces must be applied to the axle which is in equilibrium with tangential reaction forces in the contact area. It is important to realize from the outset that the existence of slip does not necessarily imply that sliding occurs everywhere in the area of contact. To illustrate this, the effect of a constant side force acting at right angles to the plane of a wheel with no rolling friction is shown diagrammatically in Figure 1, where the area of contact is seen through the track. It has been assumed in drawing this diagram that suitable restraints keep the direction of the axle constant and that the coefficient of friction is infinite. Figure 1, a, shows the stationary wheel deflected by the force *S*. The distortion produced by the side force is indicated by the dotted equatorial line. If now the wheel is made to roll a short distance towards the left, the deflection of circumferential elements coming into

* Reprinted from the *Proceedings of the International Rubber Conference*, Washington D. C., November 1959, pages 142-148.

contact with the track follows, for reasons of continuity⁶, the shape of the equator in the free region of the circumference immediately in front of the area of contact. The contact becomes kidney-shaped, as shown in Figure 1, *b* and *c*, the deflection decreasing in the front part and increasing in the rear part. The resulting asymmetrical deformation gives rise to a couple (self-aligning torque) marked by curved arrows which, however, is taken up by the restraints of the axle. When the wheel has rolled a distance comparable with the length of the contact and equilibrium has been established, the portion of the equator lying within the contact area has been distorted into a straight line making the angle

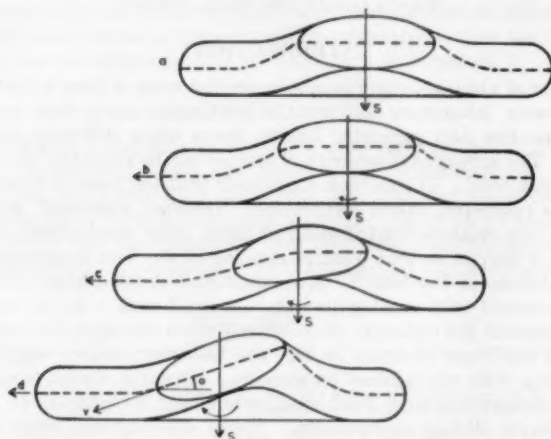


FIG. 1.—Reaction of a rolling wheel vs. a constant side force, infinite coefficient of friction.

θ with the plane of the wheel, as shown in Figure 1, *d*. The path of the leading edge of the contact coincides at all times with the travel of the wheel so that the traveling velocity v has an axial slip component Δv given by Equation 1

$$\Delta v = v \cdot \sin \theta \quad (1)$$

This motion will be referred to as crab walk.

The slip is achieved without sliding. Every element of the circumference adheres to the track while in the contact area, because of the infinite coefficient of friction. The tangential stress must increase with increasing distance from the leading edge of the contact, because the deflection follows this course. With a finite coefficient of friction, sliding will therefore set in near the rear edge as is demonstrated by the model experiment shown in Figure 2, *a*, in which a small, solid wheel rolls over a transparent track at constant slip angle. The freely rolling wheel is shown in Figure 2, *b*. Comparing Figures 2, *a*, and 1, it is seen that linearity of the equator is maintained only in the front part of the contact; near the rear edge a point is reached (limiting point) where the elastic stress exceeds local limiting friction and the circumference begins to slide back over the track.

Circumferential slip is produced by driving or braking torques. In this case, the slip velocity is equal to the arithmetical difference of traveling and the

circumferential velocity V

$$\Delta v = v - V \quad (2)$$

The effect of a braking torque is shown in Figure 2, c. An element of the circumference enters the contact in extension and while it adheres to the track the corresponding shearing strain increases again with increasing distance from the

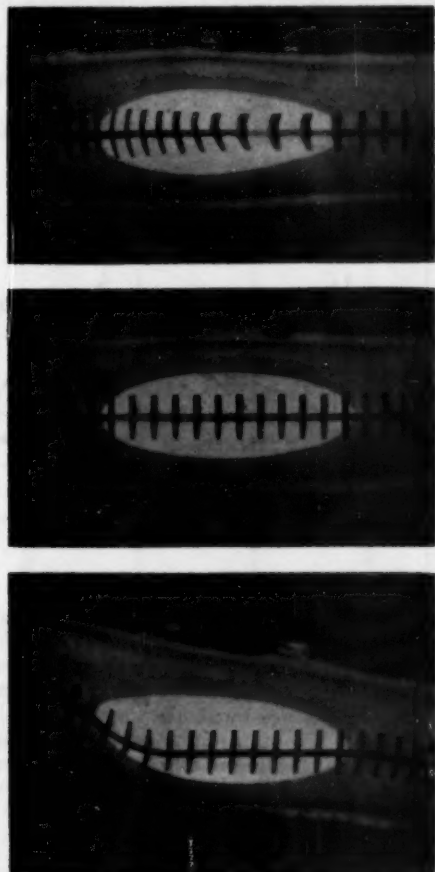


FIG. 2.—Model experiments illustrating sliding of slipping wheels. a. Crab walk. b. Free rolling. c. Slip due to braking torque. Traveling direction toward the left.

leading edge. When the stress reaches limiting value, the elements slide forward as seen from the close spacing of the lateral markings in the rear part of the contact. With a driving torque, the circumference is compressed on entering the contact and expands behind the limiting point.

As no wear occurs without sliding, the conclusion must be drawn that wear of slipping wheels is, in general, confined to the rear portion of the area of contact, irrespective of the type of slip present.

THEORY OF SLIPPING-WHEEL ABRASION

Making the assumption that the abrasion of a slipping wheel is proportional to frictional energy dissipation, neglecting strains produced by the flattening of the wheel in the area of contact and neglecting the rolling resistance, the general Equation 3 can be derived for the wear A^* per unit distance of travel³:

$$A^* = \gamma\mu/v \int_x^a (\Delta v - y^3 V) p(x) dx \quad (3)$$

where γ = proportionality constant between abrasion and energy dissipation

μ = coefficient of friction

$y = f(x)$ = deflection of the circumference as function of position on undeflected circumference

$p(x)$ = pressure distribution per unit length of contact

a = length of area of contact

X = abscissa of limiting point.

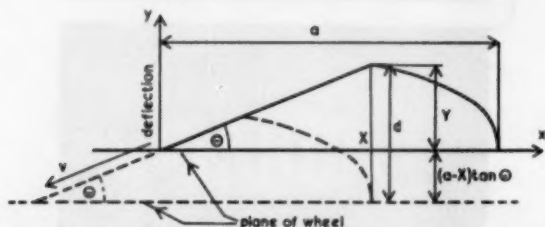


FIG. 3.—Deflection of theoretical model wheel at constant slip and resolution of sliding into its two components. a , Length of contact. d , Total sliding path. Y , Retraction sliding. $(a - X) \tan \theta$, Kinematic sliding.

Equation 3 is valid both for circumferential and sideways slip. The difficulty in solving this equation is to find the stress-strain law relating deflection y and stress in the area of contact. As this work is mainly concerned with elucidating the principal features of slipping-wheel abrasion, the real wheel or tire has been replaced by a theoretical model with the following properties: Neighboring elements of the circumference deform independently of each other and obey Hooke's law in deflection. The upper curve in Figure 3 shows the deflection of this model wheel. The deflection is zero outside the area of contact, and kinks in the curve are possible. Because of the assumptions made, Equation 3 reduces to Equation 4:

$$A^* = \gamma/v [\mu \Delta v \int_x^a p(x) dx + \frac{1}{2} k Y^2 V] \quad (4)$$

where k is a stiffness constant and y is the maximum deflection.

An interpretation of the two terms on the right-hand side of Equation 4 is given in Figure 3. After the wheel has rolled the distance $(a - X)/\cos \theta$ in the direction of v , the strain configuration has moved to the position indicated by the dotted curve. During this interval, an element which had just reached the limiting point X has slid through the distance d and leaves the area of contact. The total sliding distance has the two components $(a - X) \tan \theta$ and y

which will be called, respectively, kinematic and retraction sliding and which correspond to the two terms in Equation 4. It is seen from this equation that the contribution to the total wear by retraction sliding is given by the rate at which energy stored elastically in the adhesion range of the area of contact passes the limiting point into the sliding range where it is converted into energy of abrasion. Equation 4 presupposes therefore that the material is ideally elastic, all stored energy being recoverable as external work. This is clearly inadmissible for real materials, particularly for tire tread compounds, and allowance must be made for mechanical hysteresis losses. This has been achieved by devising manageable hysteresis loops to characterize the stress-strain be-

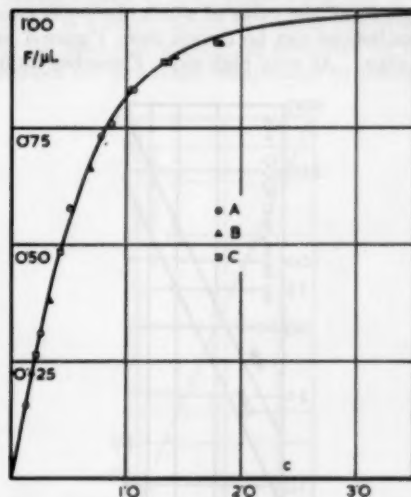


FIG. 4.—Dependence of reaction force F on slip, derived from Equations 4 and 7 for the case of an elliptic pressure distribution⁴.

havior of the wheel during cyclic deformation. The result is that for an in-completely elastic wheel the second term in Equation 4 must be multiplied with the resilience ρ so that Equation 4 becomes

$$A = \gamma/v [\mu \Delta v \int_x p(x) dx + \frac{1}{2} \rho k Y^2 V] \quad (5)$$

The relation between reaction forces and slip is as important in assessing tire wear as the relation between abrasion and slip. Given a reaction force F and slip velocity Δv , the energy dissipation D per unit length of travel of any slipping wheel is quite generally

$$D = (\Delta v/v) F \quad (6)$$

The energy dissipation is, apart from the abrasion factor γ , also given by Equation 4. Hence

$$F = A^*/\gamma s \quad (7)$$

where the slip s is defined by

$$s = \Delta v/v$$

A complete evaluation of Equation 5 has been carried out for an elliptic pressure distribution over the area of contact. We shall quote only one result by showing in Figure 4 the dependence of the reaction force F on the quantity C :

$$C = \frac{\pi}{8} k a^2 (\Delta v/V)/\mu L$$

which increases with increasing slip; L is the normal load. The force is plotted in the relative measure $F/\mu L$ the value of which obviously cannot exceed unity. Some qualitative conclusions can be drawn from Figure 4 as to the abrasion behavior at various slips. At very high slips, F reaches its limiting value, be-

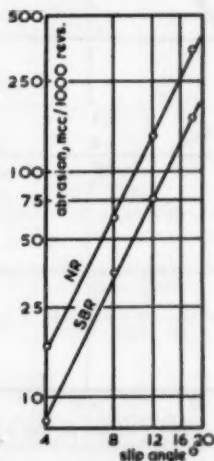


FIG. 5.—Slip dependence of abrasion on the Akron abrader.

cause the sliding range extends nearly over the whole area of contact. The first term in Equation 5 predominates, so that wear becomes independent of elastic properties, and conditions approach those of simple sliding. At low slips, however, F is proportional to the slip; also, the sliding range being short and the slip velocity small, the second term in Equation 5 predominates. Abrasion becomes proportional to resilience and, from Equation 7, increases as the square of the slip. The corresponding expressions 8 and 9 can be derived either as first approximations of the exact solutions or directly from Equations 5 and 7.

$$A_{\text{small slip}} = \frac{1}{2} \gamma \rho s^2 k a^2 \quad (8)$$

$$F_{\text{small slip}} = \frac{1}{2} s k a^2 \quad (9)$$

Eliminating the slip between Equations 8 and 9, one obtains the alternative expression, 10:

$$A_{\text{small slip}} = 2 \gamma \rho F^2 / k a^2 \quad (10)$$

It should be noted that Equations 8 to 10 do not depend on details of the pressure distribution. They contain then ormal load insofar as the length of the contact increases with increasing load.

EXPERIMENTAL VERIFICATIONS

Slip dependence of force and abrasion.—The curve in Figure 4 reproduces the essential features of cornering force characteristics of tires published in the literature⁷⁻⁹. Three sets of experimental points are marked in this graph which represent side force measurements made on the Akron abrader. Agreement with the theoretical curve has involved a suitable choice of μ and $k\alpha^2$, the latter quantity being a measurement of the effective stiffness of the wheel.

The Akron abrader is a ready means of testing experimentally the dependence of abrasion on the square of the slip, as predicted by Equation 8. Figure 5 gives results obtained for tire tread compounds of natural rubber and SBR

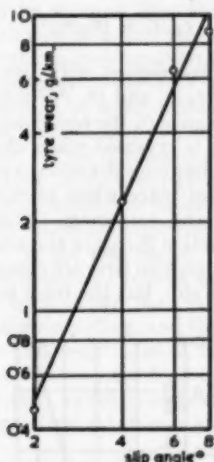


FIG. 6.—Slip dependence of the wear of a natural rubber tire¹⁰.

over a range of slip angles. The doubly logarithmic plots are straight lines with the slope 2.03, in agreement with Equation 8. Similar results have been obtained by Geesink and Prat¹⁰ with tires mounted on a special trailer. Their findings are shown in Figure 6 where the slope of the straight line is 2.14.

The influence of stiffness and traveling speed.—The abrasion ranking of two samples differing in dynamic stiffness depends on whether they are compared at equal slip or at equal force, as is evident from Equations 8 and 10. At equal slip, the ratio of abrasions is proportional to the stiffness ratio; at equal force, it is proportional to the reciprocal value of the stiffness ratio. The following experiment demonstrates the importance of this differentiation. A small trailer rolling on two standard Akron test pieces in the "toe-in" position, similar to the principle of the Akron abrader, is towed over a normal road surface. If, during each run, both samples are the same compound, and compounds are changed from one run to the other, comparison takes place at equal slip. If the two samples are different, the side forces are equal, because the trailer sets

TABLE I
COMPARATIVE ABRASION MEASUREMENTS AT EQUAL SLIP AND EQUAL FORCE
Toe-in = 15°; abrasion loss^a in cc/km

Compound	A_s	A_F	r_s	r_F	r_F/r_s	$(\theta_1/\theta_2)^2$
I	0.874	0.968	0.819	1.255	1.535	1.58
II	1.068	0.771				
III	0.752	0.872				
IV	0.748	0.652	1.005	1.340	1.330	1.25

itself automatically into this position. The samples have then, of course, different slip angles θ_1 and θ_2 , the stiffer sample running at the smaller angle. Denoting by $r_s = (A_1/A_2)_s$ the ratio of abrasions at equal slip, and by $r_F = (A_1/A_2)_F$ the ratio at equal force, one has

$$r_F/r_s = (\theta_1/\theta_2)^2$$

Table I gives the result of measurement with two pairs of compounds. The agreement between the ratios r_F/r_s and $(\theta_1/\theta_2)^2$ is satisfactory.

Table I bears out the relevance of the test conditions. In the case of compounds I and II, the ranking is reversed when changing from one method of assessment to the other. Similar considerations apply to tire testing. During normal driving, tire wear takes place when inertial forces act on the vehicle during acceleration, braking, and cornering. Under steady conditions, these forces are balanced by the reaction forces in the area of contact, as pointed out previously. If now, for example, two tires are compared on the same axle, they will necessarily have the same slip, but the total force will be divided between

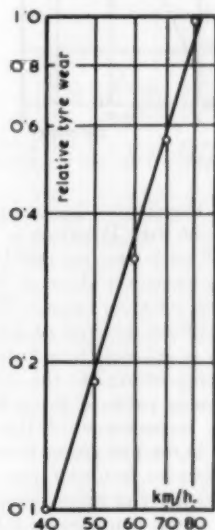


FIG. 7.—Velocity dependence of tire wear^{5, 10}.

them in inverse proportion to their stiffness. The interaction between the tires makes the harder tire appear worse and the softer tire better than they really are.

Considerations on the magnitude of the inertial forces lead to an estimate of the velocity dependence of tire wear. In cornering, which is the principal source of wear according to Gough and Shearer¹¹, the side force is equal to the centrifugal force and increases therefore with the square of the traveling velocity. Hence, wear in cornering should increase with the fourth power of the velocity. Similar estimates can be made of the effect of accelerating and braking. In practice, however, there will be a tendency to reduce speed at corners and to allow longer braking distances at higher speeds. Geesink and Prat¹⁰ have reported tire wear figures determined at various speeds under conditions where the velocity was kept as constant as possible during each run. The averages of three sets of their results, obtained with the same vehicle, have been plotted on a doubly logarithmic scale in Figure 7. A straight line with slope 3.15 is obtained. It should be stressed that this pronounced dependence of wear on speed is not so much due to a decrease in abrasion resistance, but to the need for increasing slip with increasing average speed.

The effect of mechanical hysteresis.—Figure 4, previously mentioned in connection with the slip dependence of wear, shows at the same time the large difference in the abrasion of natural and synthetic rubber when determined with a slipping-wheel abrader. This difference greatly exceeds corresponding tire wear data published in the literature. It can be shown experimentally that the effect results from the method of measurement. The same samples have been abraded on another machine employing the Lambourn principle, but imposing a large slip (-7.7) on the test pieces. Under these conditions, the abrasions of the natural and synthetic rubber are equal within the limits of experimental error. It has been shown that at large slip the mechanism of abrasion approaches that of simple sliding, and the result obtained on the high-slip Lambourn abrader is in fact very close to results of sliding experiments. The reason for using a Lambourn abrader for experiments at high slip is that the Akron abrader tends to stall at large angles. These findings dispose, at the same time, of the argument that rotation itself influences the abrasion of a test piece.

Other things being equal, the difference in apparent abrasion resistance of different polymers, such as natural rubber and SBR, when determined by slipping-wheel methods, should primarily be due to differences in hysteresis according to Equation 8. An experimental test of this theoretical result for a range of dissimilar compounds necessitates knowledge of the abrasion factor γ , that is, the relative abrasion of the samples in simple sliding. It has been shown¹² that sliding abrasion depends markedly on the nature of the abrasive so that its relative value must be determined on the same track as slipping-wheel abrasion. Experiments have been carried out with the small trailer briefly described previously, by clamping the wheels for sliding measurements. As before, a road surface was the abrasive track. An important advantage of this procedure was that road dust obviates smearing, a disturbing factor with many compounds. The resilience ρ was determined with a simple impact pendulum.

Results for nine black-loaded rubbers based on different polymers and compounded in different ways are shown in the two graphs of Figure 8. Figure 8, a, gives the abrasion in crab walk as a function of the sliding abrasion, compound E being taken as standard. It will be seen that these two groups of

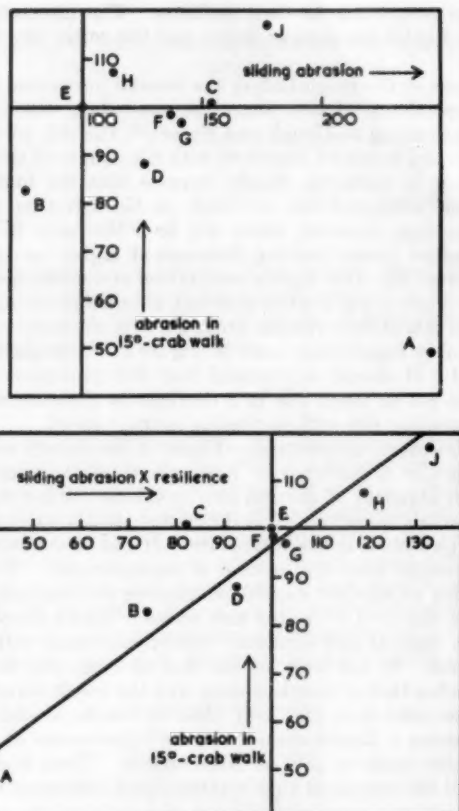


FIG. 8.—Abrasion measurements. a. In crab walk at 15° slip angle vs. sliding abrasion¹. b. In crab walk at 15° slip angle vs. the product of sliding abrasion and resilience².

data cannot be correlated, but if crab walk abrasion is plotted against the product of sliding abrasion and resilience as has been done in Figure 8, *b*, the points group themselves closely around a straight line, in qualitative agreement with Equation 8. Attention should be drawn to noticeable reversals in ranking depending on whether comparisons are made in crab walk or sliding abrasion. The most pronounced case is presented by compound A.

TABLE II
COMPARISON BETWEEN AKRON ABRASION, SLIDING ABRASION, AND THE PRODUCT (SLIDING ABRASION \times RESILIENCE) OF 3 BLACK LOADED (45 PHR) NATURAL RUBBER COMPOUNDS

	HAF	ISAF	SAF
Sliding abrasion	100	99	104.8
Akron abrasion	100	90.8	87
Sliding abrasion \times resilience	100	95.3	86.8

Figure 8 confirms the theoretically predicted importance of hysteresis in the wear process of slipping wheels for gross differences in materials and properties. Under certain circumstances, introduction of the resilience allows finer discrimination to be made, as in the influence of different filler grades. Table II gives results of measurements with three natural rubber compounds differing only in the type of black loading. Crab walk data were obtained on the Akron abrader, and sliding data on silicon carbide paper, the tracks having been dusted in both cases. Because of the similarity of the compounds, differences in abrasion patterns and their effect on abrasion could be neglected here. It appears from Table II that the superiority of the finer black is not reflected in the sliding abrasions but seems to be mainly due to the lower resilience imparted to the compound.

CONCLUSIONS

The simple theory outlined in this paper accounts for the wear of slipping wheels in their dependence on external parameters. In addition, it draws attention to the importance of the elastic properties and the unsuspected influence of mechanical hysteresis. The experimental evidence brought forward in support of this side of the theory stems mostly from laboratory work. When attempting to apply the theory to road wear, it must be kept in mind that the mechanical properties of tires are only in part determined by the tread, their elastic behavior being largely that of the pneumatic casing. Laboratory experiments carried out with solid wheels give therefore an exaggerated estimate of the influence exercised by the hysteresis of the tread on the rate of wear. Nevertheless, the relation between wear and hysteresis should be as valid for tires as for other slipping wheels, if the resilience pertaining to the tire as a whole is introduced into the calculations.

There is another aspect of hysteresis which might usefully be mentioned here. In the foregoing, the rolling resistance of tires has been neglected. While rolling resistance has most probably little effect on the wear mechanism, it does increase with increasing hysteresis of the tire. Thus, lengthening the life of a tire by increasing its hysteresis has to be paid for by an increased fuel bill.

REFERENCES

- ¹ Schallamach, A., *Trans. Inst. Rubber Ind.*, **28**, 256 (1952).
- ² Schallamach, A., *Kautschuk Gummi, Sonderheft "Der Reifen"* **27** (1955); *RUBBER CHEM. & TECHNOLOG.* **29**, 781 (1956).
- ³ Buist, J. M., Newton, R. G. and Thornley, E. R., *Trans. Inst. Rubber Ind.* **26**, 288 (1950).
- ⁴ Amon, F. H. and Dannenberg, E. M., *Rubber World* **131**, 627 (1955).
- ⁵ Schallamach, A. and Turner, D. M., *Wear* **3**, 1 (1960). References to earlier work are given in this paper.
- ⁶ Schlippe, von B., *Lilienthal Ges., Ber.* **140**, 36 (1941).
- ⁷ Förster, B., *Deut. Kraft. Forsch., Zw. Ber.* **22** (undated).
- ⁸ Joy, T. J. P. and Hartley, D. C., "Tire Characteristics as Applicable to Vehicle Stability Problems" *Proc. Aut. Dis., Inst. Mech. Engrs.* (1954).
- ⁹ Gough, R. E., *Automobile Eng.* **44**, (April 1954).
- ¹⁰ Gelaink, H. A. O. W. and Prat, C. P., *Rev. gén. caoutchouc* **33**, 973 (1956).
- ¹¹ Gough, V. E. and Shearer, G. R., "Front Suspension and Tire Wear", *Proc. Aut. Dis., Inst. Mech. Eng.* (1957).
- ¹² Schallamach, A., *Wear* **1**, 384 (1958).

POWER AND THRUST FORCE OF MILL ROLLS DURING THE MASTICATION OF RUBBER *

M. F. MIKHALEV

In this article we describe the first stage of investigations on the determination of the power needed by machines in the processing of rubber and of the magnitude of the thrust forces arising during milling as functions of the composition of the stocks, the course of processing, and the shape of the working surfaces. The purpose of the investigations in this section of the work was to establish these dependences in the mastication of natural and synthetic rubbers, a question which has not had due attention. The answers are important not only for the strength calculations of the machines, but also for reducing power consumption. This last statement is quite fully illustrated by data of Ya. Ya. Zilvestr⁸, according to which stock preparation requires up to 55% and calendering up to 30% of the total electrical energy consumed.

A number of articles^{2, 3, 7, 9, 10, 12-5} fail to answer fully the questions raised in practical experience, while the calculation methods proposed do not find application on account of the debatable nature of the assumptions on which the formulas have been based, or else on account of incompleteness.

Thus, for instance, in 1939 Kuznetsov published an article¹⁰ in which for the first time formulas were derived theoretically for the calculation of the normal and tangential forces taken up by the mill rolls. Making use of available experimental data¹⁴ Kuznetsov recommends the following equations for the determination of the thrust forces

$$P_p = P_s = A \frac{1+K}{2 \cdot K} V^2 q \left(\frac{235}{\sqrt{n}} + 27 \right) (26.8 + 0.47 D_o) L \quad (1)$$

$$T_p = B \frac{0.5K+1}{1.5 \cdot K} \cdot \frac{V}{K} \cdot \frac{1}{Pl} \left(\frac{235}{\sqrt{n}} + 27 \right) (26.8 + 0.47 D_p) L \quad (2)$$

$$T_s = B \frac{0.8K}{2 - 0.2K} \cdot \frac{V}{K} \cdot \frac{1}{Pl} \left(\frac{235}{\sqrt{n}} + 27 \right) (26.8 + 0.47 D_s) L \quad (3)$$

Here A and B are experimental coefficients

V the peripheral speed of the back roll, in m/sec

K the friction

D_o the conventional diameter of the rolls, in cm; $D_o = \frac{D_p + D_s}{2}$

n the gap factor, $n = \frac{D}{S}$

S the gap between the rolls, cm

L the length of the working part of the rolls, in cm

P_s and P_p the normal forces on the back and front rolls respectively, kg

* Translated by R. J. Moseley from *Trudy Leningrad Tekh. Inst. im. Lensoveva*, No. 38, 228-37 (1957);
a RABRM translation.

T_s and T the tangential forces on the back and front rolls respectively, kg
 Pl the Karrer plasticity
 q the specific gravity.

In deriving these formulas Kuznetsov arbitrarily identified the state of the stock in the gap as that of a dense incompressible fluid having a high coefficient of viscosity. The coefficients A and B , as the author himself admits, remain unknown, and for their determination there is required the accumulation of "a large body of experimental data which is not at present available". And finally, it follows directly from these formulas that the thrust forces P_p and P_s (comprising $\approx 90\%$ of the total thrust force) over the course of the whole process should remain constant, which directly contradicts the practical experience of the marked alteration in the properties of the stock being processed which undoubtedly influence the magnitude of the thrust forces and which from the very nature of the process cannot be true.

In 1949 Maizel proposed¹² a different method of calculating these same forces by considering vulcanized rubber a plastic material having a limit of yield σ_s in which there develop during plastic deformation three main stresses; the greatest σ_1 , the average σ_2 and the least σ_3 . Furthermore, by employing the energy theory of strength, by analogy with metals, Maizel determines the beginning of plastic deformation of the stock from the equation

$$\sigma_1 - \sigma_3 = 1.15 \sigma_s.$$

By taking from the deformed material an elementary parallelepiped and comparing the equilibrium equations, after the appropriate mathematical conversions, Maizel derives a formula for calculation of the thrust forces:

$$P_p = (1 + \beta) b_n \chi \sigma_s \sqrt{\frac{R}{\Delta h} \frac{h_{H-c}}{\delta - 1}} \left[\left(\frac{h_{H-c}}{h_k} \right)^{\delta} - 1 \right] \quad (4)$$

where P_p is the thrust force, in kg

χ a coefficient, $\chi = 1.15$

R radius, cm

σ_s the limit of yield of the stock, kg/sq cm

β a coefficient, $\beta = \frac{c_s}{b_n}$

b_n the original width of the material, in cm

b_k the final width of the material, in cm

Δh the linear reduction, in cm

$\Delta h = 2R(1 - \cos \alpha)$

α the angle of nip

h_k the final thickness of the material (the gap between the rolls), in cm

$h_{n.s.}$ the thickness of the material in the neutral cross-section, in cm

$$h_{n.s.} = h_k \left[1 + \sqrt{\frac{1 + (\delta^2 - 1) \left(\frac{h_n}{h_k} \right)^{\delta}}{\delta - 1}} \right]^{1/\delta}$$

h_n the original thickness of the material drawn into the gap, in cm;

$h_n = h_k + \Delta h$

δ a coefficient; $\delta = \frac{\mu}{\tan \frac{\alpha}{2}}$; μ is the coefficient of friction

From this formula it follows that the thrust forces are a function of the yield limit of the stock. But, as is well-known, vulcanized and raw rubber have no definite limit of yield, this being different even for one and the same grade of rubber; with some rubbers flow becomes evident, with the presence of permanent elongation, even with the initial deformations.

In addition, the measurement of σ , is not included among the ordinary technological tests of rubbers intended for processing on the mill, and consequently an extra investigation is necessary for its determination.

The determination of the yield limit of these materials is in addition hardly possible with sufficient accuracy as a result of the difficulty of measuring the true cross-section of the specimen. On increasing the gap (while keeping the nip angle constant), the thrust force decreases, as follows from the same equation⁴. In fact the inverse dependence holds good, and therefore the processing of stiff rubber and stocks is carried out always with minimum gaps and with minimum loadings, in order to prevent a sharp increase in these forces which might cause breaking of the machine.

Thus, this formula also, in addition to the conventional and debatable nature of the basic assumptions, contains a series of indeterminate factors and therefore can hardly be recommended for practical use.

In 1954 Stalinsky published articles¹³ dealing with the alteration in plasticity during mastication of natural rubber and with the determination of the energy required by the mill. These articles describe adequately the essentials of the mastication process and derive an equation for the determination of the amount of energy needed for its accomplishment

$$A = K_p \left(\frac{2K\sqrt{\tau}}{\sqrt{n}} + Pl_m\tau \right) \quad (5)$$

where K and K_p are constants

n the number of revolutions of the roll, in rpm

τ the mastication time, in min

Pl_m the plasticity for very high values of $n\tau$

Nevertheless the use of Formula (5), tested experimentally only on laboratory mills, for the design calculation of industrial machines is impossible without prior determination of a correction which takes into account the difference in the dimensions of these machines. In addition, the formula is confirmed experimentally only for natural rubber.

The work just reviewed in general exhausts all the material dealing with the calculation of the thrust forces and the energy required by the mill roll in the processing of stock. From the brief analysis we are forced to conclude that the question has not been studied sufficiently and that a general solution is lacking, thus ruling out the practical use of the proposed methods of calculation.

The first stage of the present investigation was the study of the dependence of the change in Karrer plasticity, ΔPl , upon the time of mastication τ , the condition of the rubber when added to the mill, the peripheral velocity of the roll V , the gap between the rolls i and the friction ratio F .

Treating this dependence by the method of dimensional analysis we obtain the following equation

$$\Delta Pl = A \left[\frac{V\tau}{i} \right]^b F^c \quad (7)$$

Replacing the product $V\tau$ by $\pi Dn\tau$ and substituting in place of $n\tau = M$, i.e., the number of revolutions of the mill necessary to get a given plasticity, or the number of passes of the rubber through the working contact, we bring Equation (7) to the following form

$$\Delta Pl = K \left[M \frac{D}{i} \right]^b F^* \quad (8)$$

To determine the coefficient K and the indexes we carried out a large number of experiments on laboratory and production machines.

In carrying out these investigations the peripheral velocities of the rolls were varied from 6.28 to 18.84 m/min, the gaps between them from 0.3 to 2.5 mm, the friction ratio from 1 to 3, the mastication time up to 60 min, the temperature of the rolls was kept in the limits 35 to 45°, and that of the rubber from 70 to 85°.

In our equations for the determinations of ΔPl , N and P we adopt the following designations:

V the velocity of the fast-running roll, in m/min

n the number of revolutions of the fast-running roll, in rpm

D the diameter of the fast-running roll, in m

i the gap between the rolls, in m

τ the time of plasticization, in min

L the width of the strip of rubber on the rolls, in m

ω the angular velocity of the fast-running roll, 1/sec

γ the specific gravity of the raw rubber, kg/cu.m

d the roll diameter of the laboratory mill, $d = 0.2$ m

N the power of the machine, in kW

p the thrust force

Pl_0 the initial plasticity of the rubber

F the friction ratio, the ratio of the velocities of the fast and slow rolls

As a result of the graphic analysis of the data we obtained a series of equations for the types of synthetic and natural rubber used most widely in industry.

1. For butadiene-nitrile rubber

$$\Delta Pl = K \left(\frac{D}{i} M \right)^{0.5} F^{0.87} \quad (9)$$

The coefficient K as a function of the initial plasticity and grade of rubber has the following values:

Grade	Pl_0	K
SKN-40	0.05-0.15	0.00113
SKN-26	<0.05	0.00076
SKN-18	0.05-0.25	0.000835
	0.05-0.15	0.000446

2. For styrene-butadiene rubbers

$$\Delta Pl = K \left(\frac{D}{i} M \right)^{0.7} F^{0.87} \quad (10)$$

Here K again depends upon the grade of rubber, as follows:

Grade	Pl_0	K
SKS-30	0.05-0.15	0.00005
SKS-10	0.05-0.15	0.000036

3. Natural rubber with $Pl_0 = 0.02$ to 0.1

$$\Delta Pl = 0.1924 \left(\frac{D}{i} M \right)^{0.18} F^{0.87} \quad (11)$$

The degree of deviation of the experimental from the calculated data, determined by the equation

$$\pm \Delta = \frac{Pl_{exp.} - Pl_{calc.}}{Pl_{exp.}} \times 100\%$$

is given in Table 1. As may be seen from this table, the accuracy with which the alteration in plasticity is given by Equation (8) is sufficient.

TABLE 1

Number of experiments	Deviation, in %
394	In the ± 8 range
148	± 8 to ± 16
29	± 16 and above

Applying the same method of dimensional analysis, we obtained equations for the determination of the power of the machine and of the thrust forces arising between the rolls.

For the determination of the useful power of the machine the equation characterizing its dependence upon the plasticity of the rubber,* its specific gravity, the angular velocity of the roll, the gap between the rolls, the diameter of the roll, the friction ratio and the width of the strip of rubber on the rolls, may be written in the following form:

$$N = (Pl, \gamma, \omega, i, D, L, F) \quad (12)$$

Note.—Certain authors^{1, 4, 5, 8, and 11} consider it a mistake to assess the physical and working properties of raw rubbers from the plasticity as determined on the Williams plastometer, since cases are known where with identical plasticity values the rubbers differ in properties and behave differently in the course of processing. The investigations of Stalinsky¹² and also our own show that the determination of N and F as a function of Pl gives satisfactory results, as well as their determination from recovery and softness.

After appropriate treatment and conversion Equation (12) takes on the following form:

$$N = A\gamma\omega D^4 \left(\frac{i}{D} \right)^s \left(\frac{L}{D} \right)^p Pl^m F^n \quad (13)$$

For the determination of the numerical values of the coefficients and of the indexes we carried out an investigation of the mastication of raw rubbers of the same grades on laboratory and production machines.

A graphic-analysis of the data made it possible to derive a series of equations for each group of rubbers; it is a characteristic feature that in this case, as pre-

viously, the resulting equations for each of the above mentioned groups differ only in respect of the values of the coefficient K . The single exception is SKN-18, in the equation for which there is a difference also in the index of the scale conversion factor $\left(\frac{d}{D}\right)$.

1. For butadiene-nitrile rubbers

$$N = K\gamma\omega \left(\frac{L}{D}\right)^{0.6} D^4 \left(\frac{i}{D}\right)^{0.1} Pt^{-0.7} F^{-0.2} \left(\frac{d}{D}\right)^{1.3} \quad (14)$$

The values of the coefficient K :

Grade	K
SKN-40	0.49
SKN-26	0.43
SKN-18	0.27 and the index for $\left(\frac{d}{D}\right) = 1.0$

2. For butadiene-styrene rubbers

$$N = K\gamma\omega \left(\frac{L}{D}\right)^{0.6} D^4 \left(\frac{i}{D}\right)^{0.1} Pt^{-0.7} F^{-0.2} \left(\frac{d}{D}\right)^{1.0} \quad (15)$$

The values of the coefficient K :

Grade	K
SKS-30	0.26
SKS-10	0.20

3. Natural rubber

$$N = 0.29\gamma\omega \left(\frac{L}{D}\right)^{0.6} D^4 Pt^{-0.9} \left(\frac{i}{D}\right)^{0.1} F^{-0.2} \left(\frac{d}{D}\right)^{1.3} \quad (16)$$

It is worthwhile noting that the value of the coefficient K in all these equations depends upon the amount of acrylonitrile in the butadiene-nitrile rubbers and of styrene in the butadiene-styrene rubbers.

From Equations (14, 15, 16) we calculated $N_{calc.}$ for each experiment.

The degree of deviation of the power required by the machine in each experiment ($N_{exp.}$) from the power resulting from equations (14, 15, and 16) determined from the equation $\pm \Delta = \frac{N_{exp.} - N_{calc.}}{N_{exp.}}$ is given in Table 2.

As may be seen from this table, the accuracy with which the power required by the machine in the mastication of rubbers is described by Equations (14, 15 and 16) is again sufficiently high.

The dependence of the magnitude of the thrust forces set up in the gaps upon the plasticity of the rubber, its specific gravity, the angular velocity of the roll,

TABLE 2

Number of experiments	Deviation, %
340	In the range ± 8
131	± 8 up to ± 16
44	± 16 upwards

the gap between the rolls, the diameter of the roll and the width of the strip of rubber on the rolls may be presented in the general form

$$P = \varphi(Pl, \gamma, \omega, i, D, L) \quad (17)$$

After appropriate treatment and conversion Equation (17) assumes the following form

$$P = A\gamma D^3 \left(\frac{L}{D}\right)^p \left(\frac{i}{D}\right)^q Pl^m \quad (18)$$

The numerical values of the coefficients and the indexes were obtained as the result of experiments carried out on laboratory mills.

The graphic-analysis data made it possible to obtain a series of equations for each group of rubbers with the introduction of a scale conversion factor (by analogy with the calculations of the power) for the transfer from laboratory to production machines. This also agrees with data from practical experience. It is a characteristic feature that again in this case the equations obtained for all the synthetic rubbers under investigations differ only in respect to the coefficient K . The single exception is SKN-18, the equation for which differs also in the values of the index of degree for the scale conversion factor.

1. For butadiene-nitrile rubbers

$$P = K\gamma \left(\frac{L}{D}\right)^{0.7} D^3 Pl^{-0.4} \left(\frac{i}{D}\right)^{0.1} \left(\frac{d}{D}\right)^{0.8} \quad (19)$$

The values of the coefficient K

Grade	K
SKN-40	665
SKN-26	470
SKN-18	335 and the index for $\left(\frac{d}{D}\right) = 0.6$

2. For butadiene-styrene rubbers

$$P = K\gamma \left(\frac{L}{D}\right)^{0.7} D^3 Pl^{-0.4} \left(\frac{i}{D}\right)^{0.1} \left(\frac{d}{D}\right)^{0.8} \quad (20)$$

The value of the coefficient K

Grade	K
SKS-30	375
SKS-10	300

3. Natural rubber

$$P = 190\gamma \left(\frac{L}{D}\right)^{0.7} D^3 Pl^{-0.8} \left(\frac{i}{D}\right)^{0.81} \left(\frac{d}{D}\right)^{1.1} \quad (21)$$

In the equations for the thrust forces, as in the equations for the power, the values of the coefficient K depend upon the amount of acrylonitrile in the SKN rubbers and of styrene in the SKS rubbers.

By analogy with what has gone before we calculate the value of $P_{calc.}$ from Equations (19, 20 and 21).

The degree of deviation of the thrust force in each experiment ($P_{exp.}$) from the force obtained from Equations (19, 20 and 21), determined by the equations

$$\pm \Delta = \frac{P_{exp.} - P_{calc.}}{P_{exp.}} \times 100\% \text{ is shown in Table 3.}$$

TABLE 3

Number of experiments	Deviation, in %
310	In the range ± 8
111	± 8 to ± 16
37	± 16 upwards

As may be seen from this table, the accuracy with which the magnitude of the thrust force set up in the gap during the mastication of rubbers is described by the Equations (19, 20 and 21) falls within practically permissible limits.

CONCLUSIONS

There is described the dependences of change in plasticity of rubber upon the time of mastication, the peripheral velocity of the rolls, the gap, and the friction ratio.

Equations are recommended for practical use which make it possible to determine the magnitude of the power of the machine and of the thrust forces set up in the gap between the rolls during mastication of raw rubber as a function of grade and initial plasticity.

In addition, the authors investigated the dependence of these values upon the recovery and softness of the rubbers, a characteristic feature being that the relationships of the alteration in P and N to the recovery and softness remain the same as in the case of plasticity, and differ only in respect of the values of the coefficients and indexes.

The equations describing these relationships will be considered by the authors in subsequent articles.

REFERENCES

1. Bebris, K. D. and Lisogurskii, I. Z., *Kauchuk i Resina* No. 11, 16 (1940).
2. Borodina, I. V. and Nikitin, A. K., "Properties of Soviet Synthetic Rubbers", Goskhimizdat, 1952.
3. Gelfrekh, S. V., "On the intensification of operation of calenders in the rubber industry", dissertation, Moscow Inst. Chem. Machinery Construction, 1955.
4. Evstratov, V. F., Relkh, V. N. and Sukhotina, Yu. A., *Kauchuk i Resina*, 1941, No. 4, 23.
5. Zalenkov, N. A., *Kauchuk i Resina* No. 7, 49 (1939).
6. Zilvestr, Ya. Ya. and Zyntov, A. A., "Rubber Production Machinery", Goskhimizdat, 1946.
7. Zmii, P. N. and Barskov I. M., "Machines and Apparatus for the Rubber Industry", Goskhimizdat, 1951.
8. Ivanov, A. A., *Kauchuk i Resina* No. 6, 25 (1938).
9. Kosulin, N. A., "Hydrodynamic theory of the processing of paint pastes on mills", dissertation for doctorate, Leningrad Lenseveta Technical Inst., 1954.
10. Kuznetsov, A. N., *Kauchuk i Resina* No. 11, 35 (1938); No. 3 (1939); No. 7, 33 (1939).
11. Kusov, A. B., "Investigations in the field of physico-chemical properties of vulcanised rubber", dissertation for doctorate, Leningrad Lenseveta Technical Inst., 1954.
12. Malsel, M. M., Barakov, I. M., Breitvelt, K. V. and Revieh, A. O., "Machines and Apparatus for Production of Artificial Leather", Gisleprom, 1949.
13. Stalinsky, E., *RUBBER CHEM. & TECHNOL.* 28, 606 (1955).
14. Stringfield, R. B., *India Rubber J.* 69, No. 4, 14 (1925).
15. van Rossum, A. et al., *Trans. Inst. Rubber Ind.* 25, 43 (1949).

MICROHARDNESS TESTING, ITS POSSIBILITIES AND LIMITATIONS *

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INTRODUCTION

The idea of designing a rubber hardness test instrument on a reduced or micro scale appears first to have been suggested by the Netherlands delegation at the meeting of the Rubber Committee ISO/TC45 of the International Organization for Standardization at The Hague in September, 1949. At that meeting a resolution was passed to the effect "that member countries be asked to consider the development of a microhardness tester."

This proposal was taken up actively by the late Dr. Stefano Oberto of the Pirelli Company. At the next ISO/TC45 meeting in Akron, Ohio, in October, 1950, he submitted a document describing a microhardness testing instrument, and delegations were asked to carry out experimental work with a view to further consideration of the subject at the 1951 meeting. At this meeting, held in Oxford, further documents describing the Italian work were submitted and Dr. Oberto was congratulated by all the delegations on the work he had done in presenting the details of his instrument. With characteristic modesty Dr. Oberto said he did not think he had fully met the requirements stated by the Netherlands delegation, as it was still not possible to measure hardness on products less than 0.5 mm thick; also, the instrument described was useful only for laboratory purposes and therefore unsuitable for wide distribution. Indeed, it does not yet seem that we can claim to have met fully the challenge first put to us in 1949.

However, the problem was taken up by workers in the Netherlands, Switzerland, and the United Kingdom as well as Italy, and the results presented in this paper are largely the outcome of these investigations initiated by the ISO Committee.

PURPOSE OF MICROHARDNESS TESTS

The basic reason why a micro test is needed is the fact that the measurement of the hardness of rubber by an indentation test always depends more or less on the thickness and to a lesser extent on the lateral dimensions of the testpiece. Other things being equal, this effect of thickness variation is less the smaller the indenter and the shallower the penetration. However, even with the relatively small indenting ball adopted in the ISO¹, ASTM² and British Standard³ methods (2.38 to 2.50 mm) the standard testpiece has to be 8 to 10 mm thick and with lateral dimensions 20 to 25 mm at least.

In testing manufactured articles it is often impossible to obtain from them such a large testpiece, and measurements have perforce to be made on pieces

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considerably thinner and smaller. If the standard test procedure is used on such thin or small pieces the true hardness in International Rubber Hardness Degrees (IRHD) can only be deduced by applying a thickness correction; the evidence at present available indicates that these corrections are different for different rubbers, certainly for different types of polymer, and as the correction for very thin testpieces is quite large this procedure cannot be accurate.

There is thus a serious limitation to the use of the standard hardness tests on manufactured articles and hence a need for a new form of test that can be used on very small or thin articles of those having only a small area of flat surface suitable for test, but which will nevertheless give readings directly in the accepted international units.

PRINCIPLE OF THE MICROHARDNESS TEST

The principle adopted by Dr. Oberto was the very simple one of scaling down the standard test, that is, reducing all linear measurements in the same ratio (actually 6:1), which necessitates also reducing the indenting loads in a ratio corresponding to the square of the scale factor, that is, 36:1. This means that in theory the micro test should give the same results on a testpiece about 1.5 mm thick as the standard (macro) test gives on the standard thickness of 8-10 mm.

The indentation produced by the small indenter, actually an 0.40 mm ball in Dr. Oberto's instrument, and using the indenting loads of 0.83 g initial and 15.7 g total, is thus one-sixth of that obtained in the standard test and therefore has to be multiplied by 6 before converting it to IRHD by the standard table as given in the ISO Recommendation¹ and in the British Standard² and ASTM³ procedures.

MECHANICAL PROBLEMS IN DEVISING A MICRO TEST

In scaling down the standard test by a factor of the order of 6:1 two major problems arise: firstly, the avoidance of friction and other sources of error in the indenting load; secondly, the accurate measurement of the very small movement of the indenter.

Avoidance of errors in loads.—Using the 6:1 scale factor for linear dimensions and hence 36:1 for loads, the tolerances as at present specified for the indenting loads, especially the initial load, become very small when converted to the micro scale.

	Standard (Macro)	Micro
Tolerance on initial load (ASTM ³ and BSI ²)	±1 g	±0.028 g
Tolerance on total load (ASTM ³)	±2 g	±0.055 g
Tolerance on total load (ISO ¹ and BSI ²)	±5 g	±0.14 g

It is quite clear that with the usual method of attaching the indenter to the stem of an ordinary dial micrometer gage containing a light spring acting on the stem, it would be impossible to keep within these tolerances owing to friction and the variation of the spring pressure with movement of the stem. The following means have therefore been adopted to avoid this source of error in the load.

In all instruments the acting loads are dead weights, with no springs involved. In the Oberto⁴ and the Nash and Thompson⁵ instruments, friction in the vertical movement of the indenter shaft is minimized by the use of bearings

made of polytetrafluoroethylene. In the Wallace instrument⁶ the indenter is supported in a completely frictionless manner on two pairs of leaf springs, with no bearings of any kind (see Figure 2); all measurements are made at the "null" or free floating position, so that the effective loads are exactly those added.

Measurement of movement of indenter.—In the standard test, readings of the penetration to the nearest 0.01 mm are adequate and hence a dial micrometer gage can be used. However, as the micro test requires readings almost to 0.001 mm this becomes beyond the powers of this type of gage and all micro forms of hardness test instrument have therefore had to adopt other means.

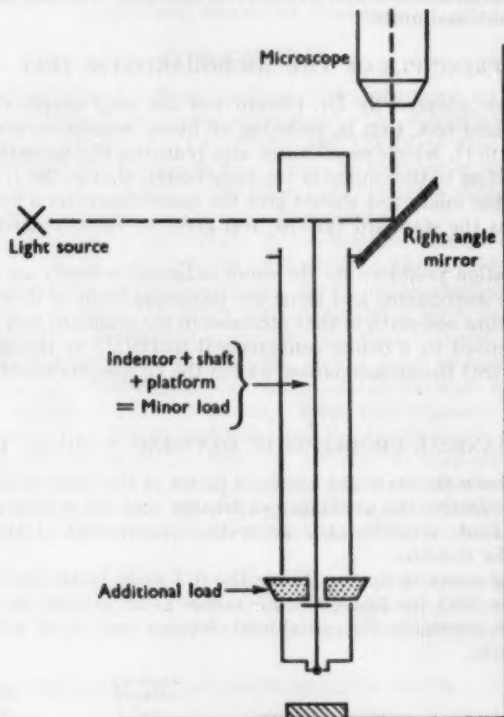


Fig. 1.—Nash and Thompson microhardness tester. (Principle of operation.)

In the original Oberto design⁴ the movement of the indenter was followed on a graticule in the field of a microscope focused on the pointed top of the indenter shaft. In the Nash and Thompson instrument the microscope uses a 45° angle mirror to swing the light path through a right angle (see Figure 1). This, although giving a more compact design, has introduced a number of optical and mechanical difficulties. In the Oberto instrument traversing of the microscope up and down can be used to compensate for any bodily movement of the foot resting on the test specimen. A second pointed shaft attached to the foot but adjacent to the top of the indenter shaft can be set to the zero of the graticule by this means, and also this zero adjustment can be made with

the minor weight on, thus allowing the use of a graticule graduated directly in IRHD. Neither of these adjustments is possible in the Nash and Thompson instrument, since there are no facilities for traversing the microscope, or (what would be more convenient) a traversing graticule. However, undoubtedly the most serious disadvantage of these optical systems is that it is not possible to read nearer to than 2 or 3 IRHD in the range 60 to 100 due to the indistinctness of the image (see Figure 5).

In the Wallace instrument (Figure 2), the movement measured is the traverse of the table (carrying the test specimen) required to take the indenter back to its null position mentioned above. This movement can be carried out in a precise manner by a fine pitch screwthread, and is also very convenient in that it can be made through a 6:1 precision wedge. The movement of the

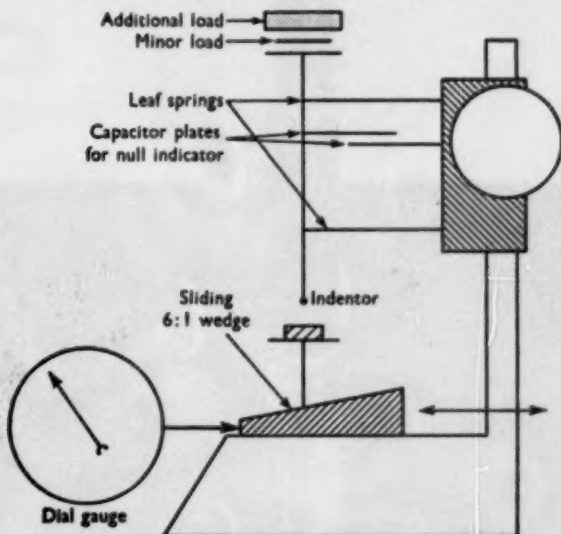


FIG. 2.—Wallace microhardness tester. (Principle of operation.)

wedge, six times that of the table, thus registers on the standard dial gage already figured in International Rubber Hardness Degrees, and thus automatically compensates for the indentation being one-sixth of that in the standard test. The null position is indicated as the balance point of a modified Wheatstone bridge circuit with the variable capacity operated by the up-and-down movement of the indenter. The traditional headphone can be used to detect this null position quite satisfactorily, but an improvement is a visual indicator consisting of a micro ammeter and associated electric circuit. This gives a very clearcut zero between two sharp maxima; not only is it less tiring than a whistling headphone, but it gives a better indication of the position of the indenter at any time.

Schematic diagrams of the Nash and Thompson and Wallace instruments showing the mode of operation are given in Figures 1 and 2, while the instruments themselves, the Wallace with the visual null indicator referred to above, are shown in Figures 3 and 4.

EXPERIMENTAL STUDIES

Equivalence with macro test.—The first question to be studied is whether the scaled-down micro test does in fact give the same hardness values as the standard or macro test. In these comparisons we must, of course, use the micro test

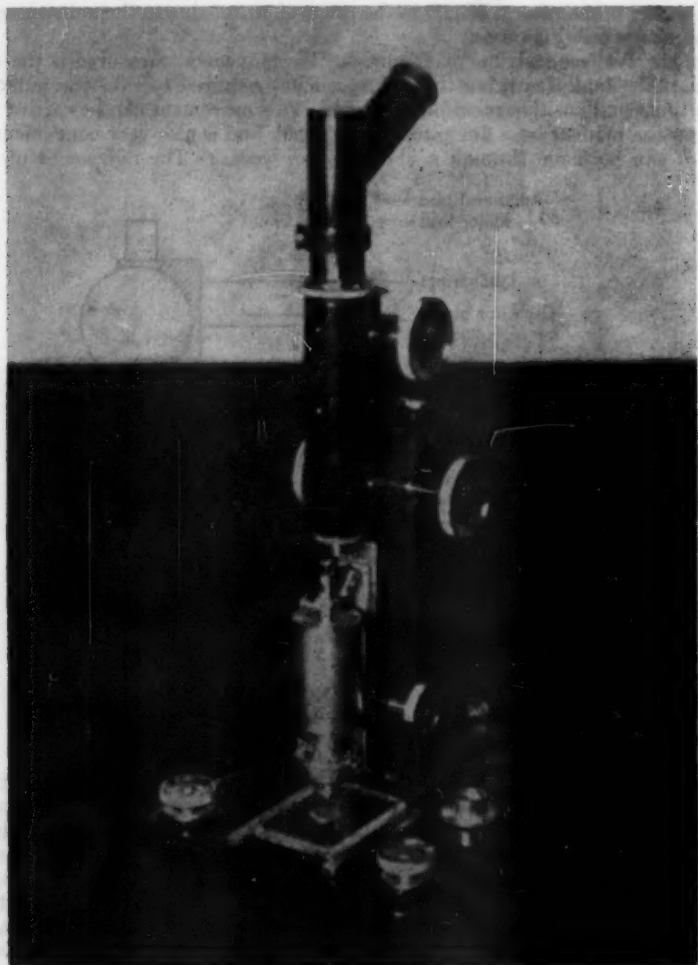


FIG. 3.—Nash and Thompson microhardness tester.

on specimens one-sixth of the thickness of those used in the standard test. Dr. Oberto presented data⁴ comparing micro readings on 1.3 mm thickness with standard test readings on 8 mm, and found no significant difference between the two except perhaps on rubbers of hardness above 65 IRHD where the micro test appeared to read one or two degrees higher.



FIG. 4.—Wallace microhardness tester.

Only one detailed study (of the Nash and Thompson instrument) has been published on evaluation of micro hardness testers (Morris and Holloway⁵), although a large amount of unpublished data has been accumulated for ISO, and the Research Association of British Rubber Manufacturers has had considerable experience in the use of both types of instruments.

All this evidence verifies the general statement that the micro test is equivalent to the macro test, i.e., it gives substantially the same value of measured hardness although in reaching a conclusion as to their absolute equivalence there are complicating factors, chief of which perhaps is the possible slight difference in state of cure between large and small rubber pieces even vulcanized under as nearly identical conditions as possible. The main use of these micro instruments will be for small complicated moldings on which it is quite impossi-

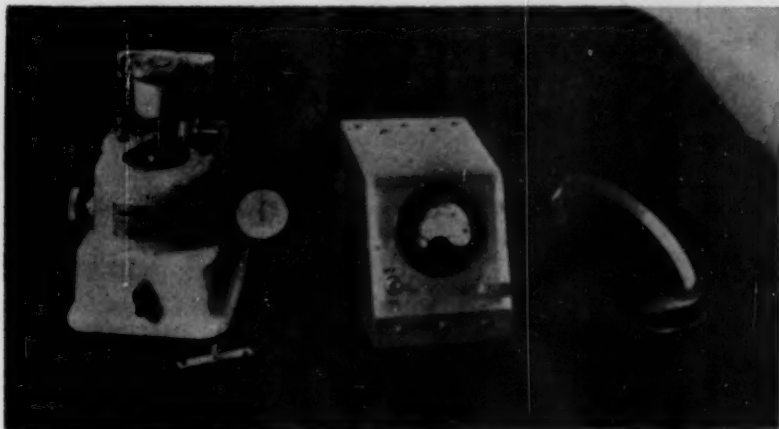


FIG. 5.—Microscope graticule and pointers, with IRHD scale.

ble to carry out the standard macro test, so that it is not possible to compare directly the micro and macro test values. The best one can do is therefore to compare the two types of test on flat parallel-sided laboratory testpieces.

The data referred to above are summarized in Figure 6; these relate to three rubbers (natural, butyl and nitrile) and include results obtained in six laboratories using the two forms of instrument; standard specimens were 9 to 9.5 mm and micro specimens 1.5 to 1.7 mm thick. The figure shows the straight line representing exact equivalence between micro and macro tests: the average

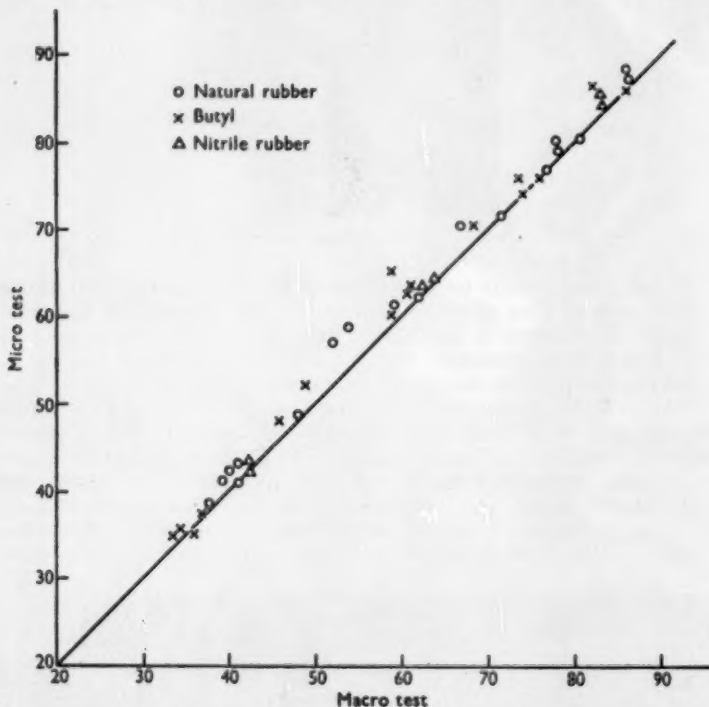


FIG. 6.—Comparison of micro and macro test results.

deviation from the line is 1.7 IRHD, independent of the hardness of the rubber. According to these results, therefore, the micro test tends to give slightly higher (harder) readings, even though the test specimens for the two forms of test were vulcanized simultaneously using a long curing time (50 to 60 minutes) so that one would have expected equality of cure.

There is in Figure 6 a certain scatter of the points about the best straight line that can be drawn through them: this is represented by a standard deviation of 1.4 IRHD, an amount which can be accounted for by the known experimental error of hardness measurements⁷.

To investigate more fully the small differences between micro and macro tests shown by Figure 6, additional experiments were made. For this purpose discs 1.5 in. diameter and 0.38 in. thick of four natural rubber compounds were

molded with small tags 0.25 in. wide and about 0.06 in. thick, thus giving as near equivalence of cure as possible. Results of measurements on these specimens are given in Table I. Macro tests were made on the standard Wallace instrument giving hardness in IRHD; micro tests on the Wallace micro instrument, both without a foot ("Baseplate" test) and also fitted with a foot (as described below).

The difference in readings between the foot and baseplate methods is discussed more fully below, but it will be noted that the foot method always gives a slightly higher reading. On the micro specimen the difference is quite small, 1 degree or less (for these flat parallel-sided specimens), but it is greater for the macro specimen. This is in agreement with the general experience that it is not advisable to test large pieces with a micro test instrument because of the inherent difficulty of making sure they are seating properly; even when using a foot there is a danger of overhanging the specimen table on the Wallace instrument.

Again, it is found that in comparing the micro test on the micro specimen with the macro test on the macro specimen, the former gives slightly higher results, by about 1 degree on the average.

TABLE I
ALL FIGURES ARE IN IRHD

Rubber	Macro tests	Micro tests			
		Macro specimens		Micro specimens	
		Baseplate	Foot	Baseplate	Foot
A	37½	36½ (-1)	38 (+½)	38 (+½)	39 (+1½)
B	48	46 (-2)	48½ (+½)	48 (0)	49 (+1)
C	62	60 (-2)	62½ (+½)	62½ (+½)	63 (+1)
D	71½	71½ (0)	72 (+½)	71½ (0)	72 (+½)

It may thus be taken as established that the macro and micro tests are for all practical purposes (though perhaps not *exactly*) equivalent on testpieces that have smooth, flat, parallel top and bottom surfaces. Such a testpiece is being called for in the new draft procedure for microhardness submitted to ISO/TC45 and adopted as the British Standard⁸. If the surfaces do not conform to the above requirement the reading will not, in all probability, be International Hardness Degrees but only a value of hardness relative to the rubber and the shape of the testpiece.

The equivalence between the micro and macro tests implies, of course, that the former test is made on a thin testpiece, i.e., about one-sixth of the thickness used for the macro test; otherwise the equivalence will not be exact.

Reproducibility of readings.—A second important point is whether the micro test is capable of giving as good reproducibility between repeat results as the standard test. The evidence is quite satisfactory on this point, since the results of direct comparative tests show that the variation between means of four readings each, expressed as standard error, is exactly 1.2 IRHD in both forms of test. It can therefore be concluded that the micro and macro tests have identical experimental errors.

The agreement between the levels of results obtained in different laboratories is also good, the variation between laboratories being in one case studied not significant and in two other cases represented by standard deviations of 0.8 and 1.1 IRHD respectively; these figures are of the same order as have been found for the macro test, namely 0.4 to 1.5 degrees (Scott⁷).

Thickness effect.—Tests on the effect of the thickness of the testpiece in the micro test have been made on natural rubber and butyl vulcanizates of various hardnesses, covering a thickness range from $\frac{1}{8}$ to 9 mm. Results are shown in Figure 7.

For the softer rubbers the curves show the normal decrease of apparent hardness with increasing thickness, but the harder rubbers are anomalous in that there is an increase in the hardness readings between $\frac{1}{8}$ and 1 mm. This effect cannot be ascribed to random testing errors, as experiments were made in five laboratories using the two forms of micro hardness apparatus; in almost

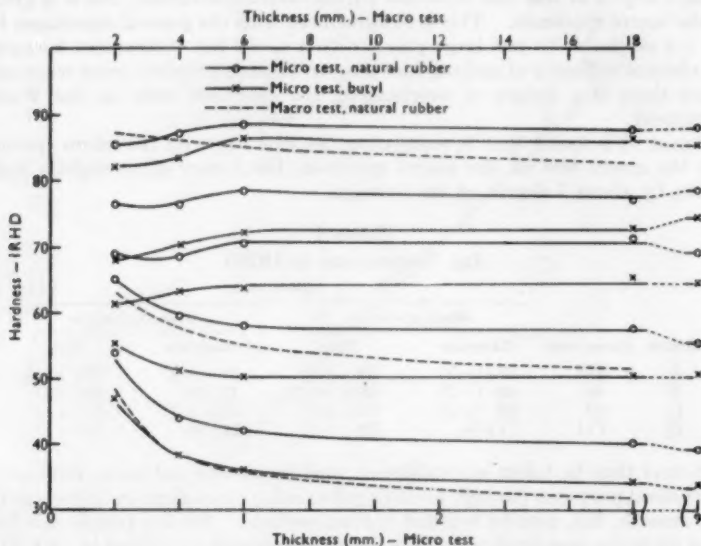


FIG. 7.—Effect of thickness of test piece.

every case the five laboratories consistently observed the rise between $\frac{1}{8}$ and 1 mm, and this increase is significant by a statistical test. The cause for this rise is still obscure, since it would be expected that the curves would fall continuously towards the right.

To compare these thickness effects with those in the macro test, dotted curves have been taken from those in the 1950 edition⁹ of BS 903 (these relate to natural rubber); these have been plotted on a thickness scale reduced in the ratio 6:1, so that theoretically the curves should be identical with those for the micro test. Although it would be too much to claim actual identity, the micro test results certainly show no greater effect of thickness than macro results, and indeed if anything, less. It seems clear, therefore, that the micro test fulfils the expectation that tests can be made on specimens only one-sixth of the thickness required for the standard test, though there is some uncertainty at thicknesses below 1 mm., for which reason the method proposed by ISO/TC45 and BSI⁸ states that thickness should not be less than 1 mm.

Lateral dimensions.—Limitations on lateral dimensions in hardness tests are not so well known or so often mentioned as thickness limitations, but nearly all

standard test methods have some limitations. BS 903: Part A7: 1957, says of the standard specimen: "no other dimension (than thickness) shall be less than 25 mm". For nonstandard specimens, of thickness less than 8 to 10 mm, the absolute minimum distance from an edge allowed is 6 mm (for 2 mm thickness)⁹. The ASTM method¹⁰ for the use of the Shore Durometer says "no hardness determination shall be made within 0.5 in. of the edge of the specimen, and in no circumstances shall hardness determinations be considered practical unless all of that area of the presser foot comprised within a radius of $\frac{1}{4}$ in. in all directions from the center of the indenter pin is resting on the specimen". All this may be summarized by saying that macro tests should not be carried out at less than 6 to 12 mm from an edge. With the micro test, scaled down 6 times, we would therefore expect 1 to 2 mm to be the limitation on accuracy.

The effect of distance from a free edge in the micro test was checked by determining hardness with the Wallace micro instrument, baseplate method, with the center of the indenter at various distances from the edge of a circular specimen 6 mm in diameter and about 2 mm thick, a short length of mm scale on the table of the instrument and the use of a hand lens enabling the distances to be assessed fairly accurately. The results for four rubbers (a) to (d) are given in Table II.

TABLE II

Distance from edge mm	IRHD			
	(a)	(b)	(c)	(d)
3	37	56	66	77
2	37	55	65 $\frac{1}{2}$	76
1 $\frac{1}{2}$	36	54 $\frac{1}{2}$	65	76
1	35	54 $\frac{1}{2}$	63	75
$\frac{1}{2}$	31	52	61	73

It will be seen that at 1 mm from the edge—something over twice the ball diameter—readings are about 2 IRHD lower, increasing to 4 to 5 IRHD low at 0.5 mm from the edge. It should be remembered also that micro tests will not normally be with standard flat specimens, but rather with O-rings and other similar small moldings. On rounded surfaces, actual distance from an edge will be quite indefinite.

Use of foot.—As in the macro test, the baseplate method, i.e. without a foot, will give wrong readings if for any reason the specimen is bodily deformed by the major load. This can happen with a bowed specimen with concave side downwards, with two or more layers superimposed, or if the lateral dimensions are of the same order as the thickness (Scott⁷). Any such deformation will be added on to the indentation and the rubber will appear softer than it actually is. The effect will be more important with the micro test, as most of its use will be on O-rings or other small awkward shaped moldings. The effect can be avoided by having a foot through which the indenter protrudes, the foot forming part of the measuring device. Thus indentation is always measured from the top surface of the specimen and any bodily movement is not recorded. The use of a foot with a micro instrument is somewhat of a drawback, in that it is not easy to see exactly where the indenter is bearing on such an awkward shaped specimen. This is particularly so with the Nash and Thompson instrument.

An improved foot attachment for the Wallace instrument, based on an original design of the National College of Rubber Technology, London, is shown in Figure 8 and mounted on the instrument in Figure 9. It consists of

a baseplate (1) which can be clamped to the rising table (9) of the instrument and attached to the baseplate a column (2) carrying an arm (3) with the foot (4). This foot is scaled down in dimensions 6 times from the macro foot and the indenter operates through the hole in the foot. The new specimen table (5) can move vertically on a cylinder (6) and a spring (7) presses it upwards, against the foot with a force of 30 g. (Note: The effective foot pressure is the difference between this spring pressure and the load on the indenter; the British Standard requires a foot pressure between 12.6 and 18.9 g, and as this should operate while the 15.7 g total indenting load is acting, the spring pressure

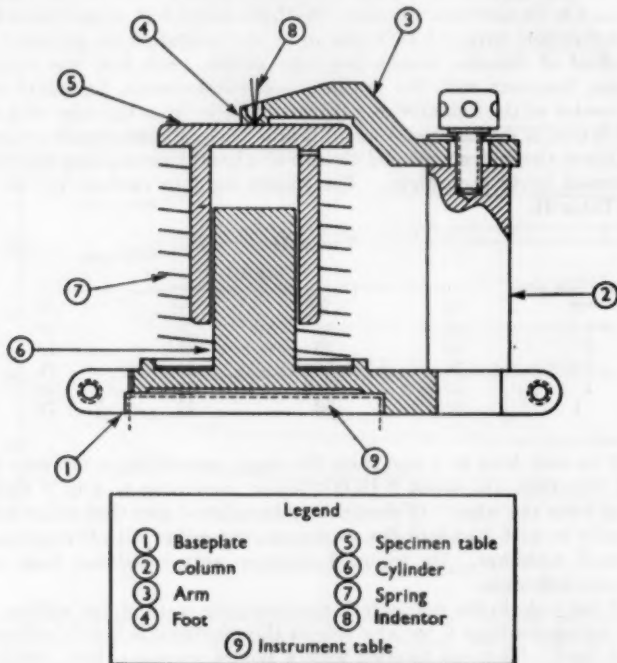


FIG. 8.—Foot for microhardness tester.

must be between 28.3 and 34.6 g.) Adjustment of the foot for concentricity with the indenter is provided by rotation of the column (2) and sliding of the arm (3) through the column, both adjustments having clamping bolts. It will be seen that the foot is rigidly attached to the measuring device, i.e. the rising table (9) of the instrument; measurements are therefore made from the *top* surface of the rubber, thus fulfilling the requirement stated above. To set the device, it is clamped on the rising table (9), the foot adjusted concentric with the indenter, and the rising head of the instrument (containing the indenting loads) locked when the tip of the indenter is just above the plane of the foot, in the null position. To use, it is only necessary to depress the spring-loaded table (5), place the specimen under the foot, raise the table (9) and foot to the null position with the minor (0.83 g) load on, set the dial gage to read 100, place

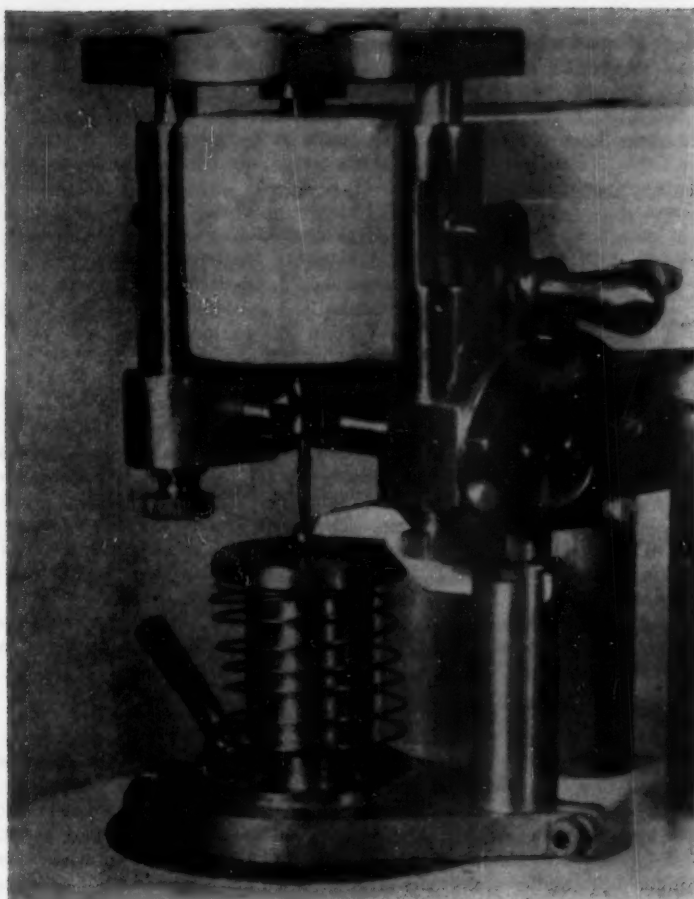


FIG. 9.—Foot mounted on Wallace microhardness tester.

TABLE III

Specimen		Baseplate		Foot	
		Side 1	Side 2	Side 1	Side 2
Sheet	1	92	91	92	92
	2	71	65	73½	72
	3	57½	56	59	58
	4	40	46	47	47
	5	38	39	39½	40
	6	27½	27	28	28
O-ring	(a)	63	—	67	—
	(b)	85	—	85	—
	(c)	77, 75, 74, 72	—	79, 80, 80, 80	—
	(d)	33	—	36	—
Cylinder		51	—	55	—

on the additional (14.85 g) load, raise to the null position again, and read the dial gage after 30 seconds. For a repeat test or a new specimen, the additional load is removed, the table lowered until the indenter is again above the plane of the foot, the specimen moved or changed and the procedure repeated. It is thus much less tedious than the baseplate test, where the head has to be adjusted up or down for thickness of specimen each time.

In Table III are given results of tests carried out by the base plate and foot methods. Specimens were as follows:

Sheets about 0.1 in. thick and 0.5 in. square.

O-rings: (a) $\frac{1}{4}$ in. section \times $\frac{1}{4}$ in. diameter.

(b) $\frac{1}{4}$ in. section \times $\frac{3}{4}$ in. diameter.

(c) $\frac{1}{4}$ in. section \times 1 in. diameter.

(d) 0.1 in. section \times 1 in. long piece.

Cylinder: $\frac{1}{4}$ in. diameter \times $\frac{1}{4}$ in. high.

The sheets were tested on both sides and the O-rings at a number of points round the periphery on one side only. Except where individual results are given, figures are the means of 4 closely concordant results. It will be seen that in the baseplate test (without foot) "flat" sheets 2 and 4 show a considerable difference on the two sides (due to slight bowing) and O-ring (c) shows a progressive change round the ring. These effects are removed by using the foot. On all specimens except O-ring (b) the foot test gives higher results (less indentation) especially for the softer molded specimens, i.e. O-rings (a) and (d) and the cylinder.

All these results are as would be expected when the specimen moves or compresses bodily under the major load. It is concluded that for the most reliable results, the foot is necessary.

CONCLUSIONS

The micro test fulfils the requirement of enabling hardness measurements to be made on specimens much thinner and smaller than those needed for the standard (macro) test. It is thus possible to obtain readings in International Rubber Hardness Degrees on specimens down to 1 mm thick and of lateral dimensions only 2 to 3 mm; reproducible measurements can be obtained even on thinner and smaller specimens, although the results would not necessarily be the true hardness in IRHD.

To get the most reliable results, especially on small pieces with nonparallel faces, the instrument should be fitted with a foot.

The micro test gives repeat results as uniform as those obtained with the macro test.

It must be emphasized that the micro test is designed for use on thin pieces of rubber, and should not be used on relatively thick pieces, on which it is, indeed, less suitable than the normal (macro) test.

SUMMARY

The need to test small awkwardly shaped rubber articles, which cannot be tested by normal methods, has led to the development of a scaled-down micro test for hardness. Attention is drawn to the mechanical problems that arise in devising such a micro test, especially those associated with friction in the

moving parts and with the measurement of the very small movements of the indenter; the various ways in which these problems have been solved are described. The results of experimental work are presented to show the substantial equivalence in readings between the micro and the normal (macro) test, the good reproducibility of micro test results, the influence of testpiece dimensions, and the advantage of using a foot on the instrument as specified in ISO Recommendation R48 for the normal hardness test.

Attention is drawn in particular to the influence of the dimensions of the rubber tested, showing on the one hand that reliable hardness measurements can be made, as expected theoretically, on much thinner and smaller specimens than in the standard test, though on the other hand there are minimum dimensions below which even the micro test cannot be expected to give results agreeing strictly with those of the macro test.

REFERENCES

- ¹ International Organization for Standardization, I.S.O. Recommendation R48: Determination of hardness of vulcanized natural and synthetic rubbers, 1st Edition, 1957.
- ² American Society for Testing Materials, ASTM Designation D1415-56T: International Standard hardness of vulcanized natural and synthetic rubbers.
- ³ British Standards Institution, B.S. 903: Part A7: 1957, Methods of testing vulcanized rubber: Determination of hardness.
- ⁴ Oberto, S., "Nuovi strumenti per la misura di durezza," *Ricerca e Sviluppo (Pirelli)*, 1954, No. 2 (October).
- ⁵ Morris, R. E. and Holloway, J. M., *ASTM Bull.* 1957, No. 222, 45.
- ⁶ Wallace, H. W., & Co., Ltd., *India Rubber J.* 127, 917 (1954).
- ⁷ Scott, J. R. *Trans. Inst. Rubber Ind.*, 27, 249 (1959).
- ⁸ British Standards Institution, B.S. 903: Part A20: 1959, Methods of testing vulcanized rubber: Determination of hardness (micro-test).
- ⁹ British Standards Institution, B.S. 903: Part 19: 1950, British Standard hardness test.
- ¹⁰ American Society for Testing Materials, ASTM Designation D676-58T: Method of test for indentation of rubber by means of a durometer.

THE DETERMINATION OF ZINC OXIDE IN RUBBER VULCANIZATES BY X-RAY DIFFRACTION *

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INTRODUCTION

Zinc oxide is a necessary component in most accelerator-sulfur vulcanization systems. While it is not an accelerator, its presence leads to increased modulus, i.e., tighter cures. The manner in which it can effect this better cure is not completely clear. Some insight into the role of zinc oxide has been gained through the analysis of the vulcanizate for reaction products of zinc, such as zinc stearate, the zinc salts of the accelerators, and zinc sulfide. However, these products may not account for all of the zinc oxide which has reacted. An analytical method for the direct determination of unreacted zinc oxide in vulcanizates was therefore needed.

The determination of zinc oxide in rubber vulcanizates has received scant attention. Wet-chemical techniques for analysis of the sample after ashing provide only the total amount of zinc from which the amount of unreacted zinc oxide cannot be determined.

Endter¹ has reported the use of the Debye-Scherrer x-ray technique for the identification of zinc oxide in rubber samples. While similar to the method developed in this laboratory, Endter employed photographic film for recording the diffraction pattern, and special sample preparation was required to accommodate the photographic technique. This method was satisfactory for qualitative identification of zinc oxide, but was difficult to use for quantitative analysis.

Subsequent to this investigation Hagino et al.² described the use of x-ray diffractometry for the determination of the mixing ratio of ingredients compounded in rubber. This method was also suggested for the quantitative analysis of zinc oxide, but no studies were reported.

During a study in this laboratory to determine the role of zinc oxide in the vulcanization of rubber, a new analytical method, based on x-ray diffractometry, was developed. The method was rapid, nondestructive, and simple. The data were reliable and accurate.

EXPERIMENTAL

MATERIALS

All materials used to prepare the vulcanized samples were commercially available. Natural rubber was No. 1-ribbed smoked sheet. The reinforcing fillers were of two types: a fine-particle, hydrated, amorphous silica, (Hi-Sil

* Presented to the Division of Rubber Chemistry, 134th Meeting of the American Chemical Society, Chicago, Illinois, September 7-12, 1958; Reprinted from the *Journal of Applied Polymer Science*, Vol. 2, pages 225-230, 1959.

TABLE I
COMPOUND RECIPES

	A, parts by weight				B, parts by weight		
	100	100	100	100	100	100	100
Natural rubber							
Amorphous silica or HAF black	50	50	50	50	0	20	50
Zinc oxide ^a	2.5	5.0	7.5	10.0	5	5	5
Curatives ^b	7	7	7	7	7	7	7
Stearic acid	0	0	0	0	3	3	3

^a Added as 50% masterbatch in natural rubber.

^b Sulfur, 3.0; MBTS, 0.8; DOTG, 1.2; TEA, 1.0; PBNA, 1.0.

233, Columbia-Southern Chemical Corp.) and a high-abrasion furnace (HAF) carbon black, (Philblack O, Phillips Chemical Co.). The zinc oxide ($\geq 99\%$ purity) was Black Label Type XX72 (New Jersey Zinc Co.). Spider Brand sulfur was used in all compounding. The remaining curing ingredients were rubber-grade products obtained from a variety of sources: MBTS (2,2'-dithiobisbenzothiazole), DOTG (di-*o*-tolylguanidine), PBNA (phenyl-2-naphthylamine), and TEA (triethanolamine).

COMPOUNDING AND VULCANIZATION

Natural rubber compounds were prepared according to the recipes of Table I. The filler and rubber were mixed in an internal mixer (Banbury-size B), and the remaining components were added on a 6 \times 12-inch rubber mill. Zinc oxide was added as a 50% masterbatch in natural rubber. After sheeting from the mill at 0.075-in. gage, the compounds were cured between aluminum foil (0.004 in. thick) in preheated laboratory presses at 142° C and 2000 psi. Immediately after removal from the molds, the cured samples were cooled in water.

DIFFRACTOMETRIC ANALYSIS FOR ZINC OXIDE

The foil was removed from the cured tensile sheets, and samples measuring 1½ \times 1½ in. on a side were cut out. The sample was placed on top of a standard x-ray sample holder made from aluminum and then inserted in the goniometer

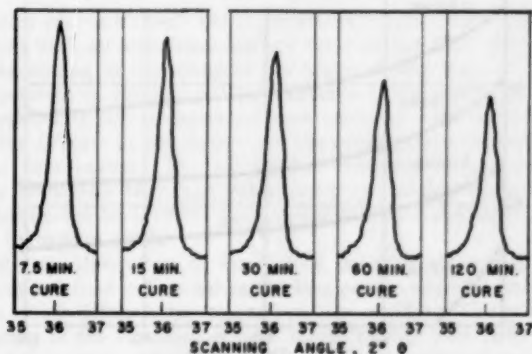


FIG. 1.—Typical ZnO diffraction patterns from a rubber vulcanizate.

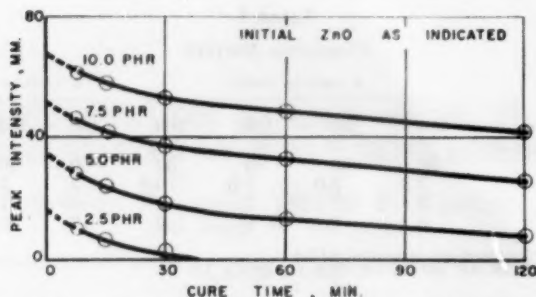


FIG. 2.—Variation in peak intensity in silica-filled vulcanizates.

for scanning. A Norelco geiger counter diffractometer employing $\text{CuK}\alpha$ radiation was used in the determinations. The conditions throughout this study were: 35 kv, 15 ma on a copper target tube, a nickel filter to remove $\text{CuK}\beta$ radiation, a 1° divergent slit, 0.006-in. receiving slit, 1° scatter slit, and the usual Soller slits to collimate the beam. The sample was scanned at the rate of $\frac{1}{2}^\circ$ per minute from an angle of 37° to $35^\circ 2\theta$, with a scale factor of 32 and a time constant of 2 sec. The variation in x-ray intensity was recorded on a strip chart. A typical diffraction pattern for a series of cures is shown in Figure 1.

The area of the sample permitted two determinations to be made on each side. From the diffraction pattern, the intensity of the zinc oxide peak above background, at an angle of $36.2^\circ 2\theta$ was measured for each determination. The average of the four measurements was then plotted against the corresponding time of cure. Smooth curves were drawn through each series of experimental points and extrapolated to zero cure time (Figures 2 and 3). The value of the peak intensity at zero cure time, obtained by extrapolation, then corresponded to the initial zinc oxide concentration. Calibration curves were obtained by plotting this extrapolated peak intensity against the initial percentage of zinc oxide (Figure 4).

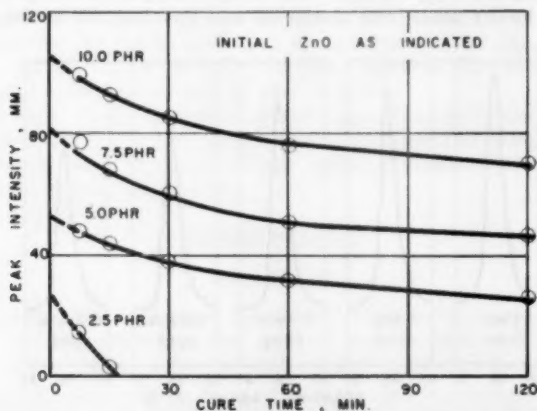


FIG. 3.—Variation in peak intensity in black-filled vulcanizates.

DISCUSSION OF RESULTS

In order to obtain the relation between the diffraction intensity and the concentration of zinc oxide, the peak intensity at known concentrations must be determined. If it is assumed that no reaction of zinc oxide occurs prior to curing, the diffraction peak intensity of the uncured rubber compounds can be used. However, attempts to obtain the diffraction pattern before curing resulted in erratic measurements. This was due to the rough surface and the soft nature of the sample, both of which prevented a uniform orientation of the specimen in the goniometer. As a result of this, wide variations of the peak intensity occurred when measuring the four different areas of the uncured sample.

The diffraction peak intensity in the uncured compounds could be estimated with reasonable accuracy by extrapolation of the peak intensity-cure time curve to zero cure time. This was done in Figures 2 and 3 for the compounds of Table IA. Though the peak intensity-cure time curves were non-

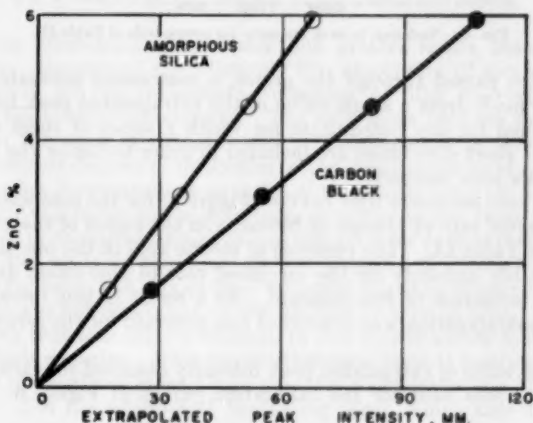


FIG. 4.—Variation of peak intensity with ZnO concentration.

linear, smooth curves through the experimentally determined points permitted extrapolation with an estimated relative error of less than $\pm 5\%$. This error will vary depending on the slope of the curve at zero time of cure. This, in turn, is dependent on the rate of disappearance of the zinc oxide.

The variation of the extrapolated peak intensity with the initial zinc oxide concentration (Figure 4) was linear, and the curve passed through the intercept of the two coordinates. The silica-filled vulcanizates had correspondingly lower peak intensities than the vulcanizates containing carbon black. This was expected on the basis of the predicted greater absorption of x-radiation by silica than by carbon black.

The differing absorption of x-radiation between silica and carbon black means, of course, that individual calibration curves must be obtained for each vulcanizate which differs in the amount or type of filler. Ordinarily this would require a study of the variation of peak intensity with zinc oxide concentration for each rubber compound which had a different degree of x-ray absorption. Since, however, the plot of peak intensity versus zinc oxide concentration was

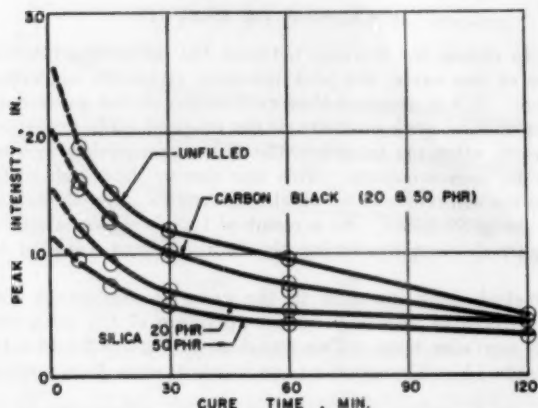


FIG. 5.—Variation in peak intensity for compounds of Table IB.

linear and also passed through the origin, a reasonably accurate calibration curve can be made from a single value of the extrapolated peak height. This can be obtained for any vulcanizate for which a series of cures is available, provided that short cure times are included in order to follow the initial rapid decrease in the peak intensity.

The peak intensity-cure time curves (Figure 5) for the compounds of Table IB had a greater rate of change of intensity in the region of the extrapolation than those of Table IA. The presence of stearic acid in the one series of compounds probably accounts for the increased rate of zinc oxide disappearance through the formation of zinc stearate. As a result of this increased rate of change, the extrapolation was somewhat less accurate for the series containing stearic acid.

The single value of extrapolated peak intensity obtained for each vulcanizate from Figure 5 was used for the calibration curves of Figure 6. Again, the

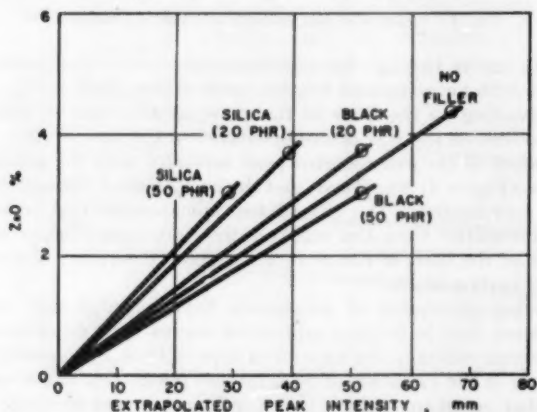


FIG. 6.—Zinc oxide calibration for compounds varying in filler loading.

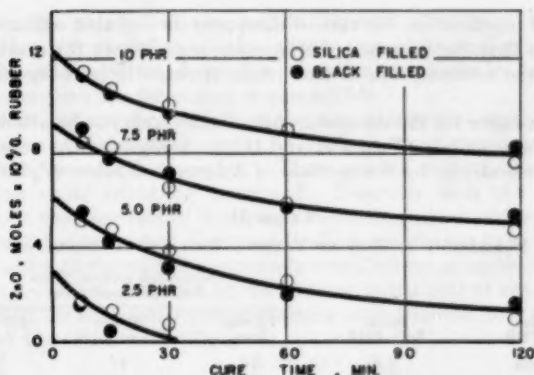


Fig. 7.—Rate of ZnO disappearance at various initial ZnO contents.

curves for the silica-filled vulcanizates had greater slopes than those with carbon black. Because of the relatively low absorption of x-rays by carbon black, the curve for the vulcanizate containing no filler was very similar to those of the black-filled vulcanizates. The differences between these could be attributed to the error of extrapolation or to variations in x-ray scattering caused by different degrees of dispersion of the small particles of carbon black.

By expressing concentrations as moles of zinc oxide per gram of rubber, we eliminated any variations due to differences in compounding ratios. Examination of the rate of change of zinc oxide concentration for each of the vulcanizates on this basis was made for the compounds of Table IA in Figure 7 and those of Table IB in Figure 8. It was at once apparent that the change in zinc oxide concentration was not dependent on the amount or type of filler.

It is known that zinc oxide is required in this type of curing system in order to obtain a high modulus. This implies that zinc oxide is instrumental in the development of crosslinks, since a high modulus is indicative of a high degree of crosslinking. Yet the addition of reinforcing fillers, which also increased the

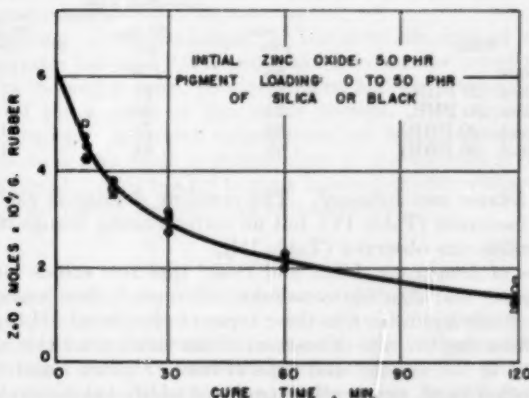


Fig. 8.—Rate of ZnO disappearance at various filler loadings.

modulus, had no effect on the rate of disappearance of zinc oxide. The point to be made is that the presence of zinc oxide is necessary for maximum crosslinking, but the consumption of zinc oxide apparently is independent of this crosslinking.

The major cause for the disappearance of zinc oxide can be attributed to the formation of zinc sulfide (Tables II and III). Analysis of the vulcanizates for zinc sulfide, essentially by the method of Adams and Johnson³, indicated that

TABLE II
FORMATION OF ZNS AT VARIOUS ZNO CONCENTRATIONS

Filler, 50 PHR	Initial ZnO, PHR	(Moles ZnS formed/Moles ZnO consumed) $\times 100$		
		7.5 min cure	30 min cure	120 min cure
Silica	2.5	34	47	71
	5.0	30	52	51
	7.5	33	52	56
	10.0	25	35	59
Black	2.5	92	77	81
	5.0	100	81	69
	7.5	100	100	88
	10.0	100	87	76

zinc sulfide accounted for 65–100% of the reacted zinc oxide in the compounds containing no filler or containing HAF black. On the other hand, only 24–77% of the reacted zinc oxide appeared as zinc sulfide in the presence of amorphous silica. Also, whereas increasing amounts of carbon black had only a small effect on the amount of zinc oxide converted to zinc sulfide, 50 PHR of amorphous silica caused a large reduction in the formation of zinc sulfide, as shown in Table III. This reduction in zinc sulfide was accompanied by a reduction in the crosslink density (Table IV), as determined by the equilibrium swelling

TABLE III
FORMATION OF ZNS AT VARIOUS FILLER LOADINGS

Filler	(Moles ZnS formed/Moles ZnO consumed) $\times 100$		
	7.5 min cure	30 min cure	120 min cure
None	88	70	75
Silica (20 PHR)	77	67	67
Silica (50 PHR)	24	39	46
Black (20 PHR)	82	73	71
Black (50 PHR)	65	64	71

technique of Adams and Johnson³. The crosslink density in the presence of carbon black increased (Table IV), but no corresponding change in the formation of zinc sulfide was observed (Table III).

If the view of Armstrong, Little and Doak⁴ that zinc sulfide formation is a measure of mono- and disulfide crosslinks is accepted, then amorphous silica (at 50 PHR) effects a reduction in these types of crosslinks. However, it does so without influencing the rate of reaction of zinc oxide since this was found to be independent of the amount and type of filler (Figures 7 and 8). Carbon black, on the other hand, apparently introduced additional crosslinks which did not result in the formation of zinc sulfide, since the presence of carbon black had

little effect on the amount of zinc sulfide formed. This may indicate that carbon black has introduced crosslinks independent of the sulfur crosslinks, or that it merely influenced the formation of sulfur crosslinks by a mechanism which did not involve the formation of zinc sulfide.

The question concerning the fate of the zinc atoms that were not utilized for the formation of zinc sulfide cannot be resolved, since complete analyses of the vulcanizates were not attempted. There remain several other reactions by which zinc oxide could be consumed. Reaction with the accelerator, MBTS, to form the zinc salt of 2-mercaptobenzothiazole would account for a part of the reacted zinc oxide. Fatty acids which are present in natural rubber or which are added to the rubber compounds would utilize an additional amount. That this did occur was indicated by the greater initial rate of reaction of zinc oxide (Figure 8) for the compounds containing added stearic acid than that in the absence of the added acid (Figure 7).

TABLE IV
CROSSLINK DENSITY AS A FUNCTION OF FILLER LOADING

Filler	Crosslink density, moles $\times 10^3$ /g of rubber		
	7.5 min cure	30 min cure	120 min cure
None	1.0	1.2	1.1
Silica (20 PHR)	1.0	1.2	1.1
Silica (50 PHR)	0.7	1.0	0.9
Black (20 PHR)	1.3	1.5	1.4
Black (50 PHR)	1.6	2.1	2.1

As Brooks, Boggs, and Ewart⁵ have shown, amorphous silica is capable of reacting with zinc stearate to liberate stearic acid which then can react with additional zinc oxide. The rubber compounds containing both silica and fatty acids thus may provide yet another means by which zinc oxide is consumed.

Though not substantiated, reaction of zinc oxide with triethanolamine or di-*o*-tolylguanidine may afford still another route for its disappearance. Zinc salts have been found to form coordinate complexes with nitrogen- and oxygen-containing compounds⁶.

In summarizing, a new technique for the determination of zinc oxide in rubber vulcanizates has been developed which involves the use of x-ray diffractometry. The method is rapid, nondestructive, and has a relative error of less than $\pm 10\%$ of the amount of zinc oxide present. The application of the technique to some typical rubber vulcanizates has demonstrated that the rate of disappearance of zinc oxide is independent of the amount or type of reinforcing filler present. This has led to some interesting observations which may aid in defining the role of zinc oxide in vulcanization.

SYNOPSIS

The important role of zinc oxide in accelerated rubber vulcanization has not been thoroughly defined. One major void in the investigations reported has been the absence of a suitable analytical method for following the rate of disappearance of zinc oxide. A method based on x-ray diffractometry is here presented for the direct determination of zinc oxide in rubber vulcanizates. The technique employed is rapid and nondestructive and has a relative error

less than $\pm 10\%$ of the amount of zinc oxide present. Application to typical accelerated rubber vulcanizates has shown that the rate of zinc oxide disappearance was independent of the amount and type of reinforcing filler. It was found also to be independent of the degree of crosslinking despite the known dependence of high level crosslink formation on the presence of zinc oxide in this type of curing system. The major part of the reacted zinc oxide appeared as zinc sulfide.

ACKNOWLEDGMENTS

The authors wish to express their thanks to the Columbia-Southern Chemical Corporation for permission to publish this work and to Drs. F. Strain, J. Bachmann, and B. DeWitt for their interest and helpful suggestions.

REFERENCES

- ¹ Endter, F., "The Quantitative and Qualitative Determination of Fillers in Vulcanizates", paper presented to the German Rubber Society Meeting, Munich, October 21-23, 1954.
- ² Hagino, Y., Hirata, Y., Yokoyama, T., and Hashizume, G., *Nippon Gomu Kyokaishi* **29**, 1033 (1956).
- ³ Adams, H. E. and Johnson, B. L., *Ind. Eng. Chem.* **45**, 1539 (1953); *RUBBER CHEM. & TECHNOL.* **26**, 741 (1953).
- ⁴ Armatong, R. T., Little, J. R., and Doak, K. W., *Ind. Eng. Chem.* **36**, 628 (1944).
- ⁵ Brooks, M. C., Boggs, F. W., and Ewart, R. H., "The Influence of the Chemical Nature of the Surface of a Filler upon its Reinforcement Properties", paper presented to the German Rubber Society Meeting, Cologne, May 7-10, 1958.
- ⁶ Sidgwick, N. V., "The Chemical Elements and their Compounds", Vol. I, p. 280, Clarendon Press, Oxford, 1930.

A METHOD OF SCREENING ANTIOZONANTS *

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The value of an organic compound as an antiozonant in rubber can be determined only by testing it in a rubber formulation under conditions to be met in service. The present state of this art has been reviewed by Biggs¹.

In a broad sense, any organic compound is an antiozonant since there are few compounds that do not react with ozone in some manner. For a compound to be a good antiozonant in rubber, however, it must prevent the reaction of ozone with the unsaturated hydrocarbons in rubber. In other words, the compound must react with ozone preferentially at a faster rate than ozone reacts with an unsaturated hydrocarbon.

The excellent reviews of Long² and Bailey³ cover the reactions of organic compounds with ozone in general with a few references to the relative rates of reaction. In one experiment by Barnard⁴, he reports the preferential reaction of ozone with octene-1 when an equimolecular mixture of this olefin and di-n-butyl sulfide were reacted with ozone. The extent of the reaction, however, is based upon infrared analysis of the products formed.

Delman, Simms, and Allison⁵ have proposed a method of evaluating the protective ability of "antioxidant chemicals" that uses the rate of change of viscosity of "polymeric solutions."

The basis of the new procedure described here is to evaluate compounds according to their inherent ability to react preferentially with ozone at a faster rate than ozone reacts with an unsaturated hydrocarbon. This type of screening evaluation effectively separates compounds into two classes—those that should be tested in rubber and those that should not.

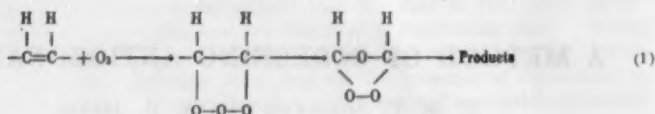
PRINCIPLE OF THE METHOD

A good antiozonant is defined as one that inhibits the olefin-ozone reaction by reacting preferentially with the ozone present. To compete successfully with the unsaturated linkage of a hydrocarbon for ozone, an antiozonant must react with ozone at a faster rate than the unsaturated hydrocarbon. The degree to which a compound can compete successfully with the unsaturated linkage of a hydrocarbon for ozone can be determined by measuring the oxygen content of a stream of ozonized air after it has passed through a mixture of the compound and an excess of unsaturated hydrocarbon.

In this method an air stream containing 21% by volume oxygen and 79% by volume nitrogen is ozonized by passing it through an ozonator. The ozonized air stream is then passed through a solution of the compound under test as an antiozonant and an excess of an unsaturated hydrocarbon, cyclohexene, in a solvent that is inert toward ozone. A control reaction is run simultaneously by passing the same stream of ozonized air through a potassium iodide solution. Measuring the effluent air streams for oxygen content determines the value of a compound as an antiozonant.

* Reprinted from *Rubber World*, Vol. 141, No. 2, pages 240-246, November 1959.

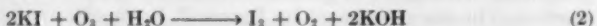
Unsaturated hydrocarbons react with ozone in the three-atom manner:



In this reaction, also known as ozonation, three atoms of oxygen are consumed, and an ozonide is formed. A measurable volumetric decrease in oxygen content also occurs.

Cyclohexene, which is used as the model unsaturated hydrocarbon in this method, reacts with ozone in the three-atom manner to form a polymeric ozonide that can be handled safely⁶⁻¹⁰. The effluent air stream from the cyclohexene-ozone reaction has the following volume composition: 18.55% O₂ and 81.45% N₂. The original air stream (21% by volume O₂ and 79% by volume N₂), in passing through the ozonator and through the cyclohexene, has undergone a decrease of 2.4% by volume of oxygen¹².

Potassium iodide, which is used as the control in this method, reacts with ozone in the one-atom manner:

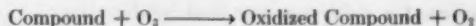


In this reaction, which serves as a model for the oxidative reaction of ozone, for each molecule of ozone, one atom of oxygen is consumed. The other two atoms of oxygen combine to form a molecule of oxygen.

The effluent air stream from the potassium iodide solution has the following percent by volume composition: 20.2% O₂ and 79.8% N₂. Compared to the volumetric content of the original air stream, the effluent stream from the KI-ozone reaction exhibits a decrease of 0.8% by volume of oxygen.

If the stream of ozonized air is passed through a solution of a compound to be tested in a solvent inert to ozone, the compound may react with the ozone in the stream in three ways:

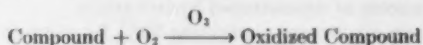
(1) One-Atom Manner—Oxidation by Ozone Alone



(2) Three-Atom Manner—Ozonation



(3) Ozone Catalyzed Oxidation by the Oxygen in the Stream



The oxygen content of the effluent from the reactor containing the compound alone should indicate which type of reaction is taking place. If the one-atom reaction predominates, the oxygen content of the effluent is similar to that obtained from the potassium iodide reaction illustrated in Equation 2. The effluent from a compound reacting in the three-atom manner should have an oxygen content similar to that obtained for the olefin-ozone reaction shown in Equation 1. If ozone catalyzes the oxidation of the compound by the oxygen

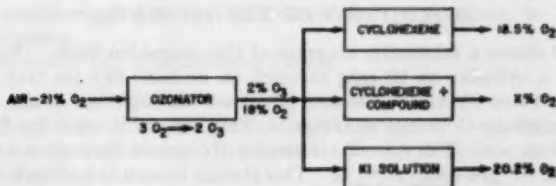


Fig. 1.—Reaction flow diagram of air through ozonator and then through the two reference trains, cyclohexene and KI solution, as well as test compound.

in the stream, the effluent has an oxygen content dissimilar to the other two. These reactions are shown in Figure 1.

Determining the manner in which a compound alone reacts with ozone is not a true indication of the value of the compound as an antiozonant in rubber. In this method, therefore, instead of subjecting the compound alone to the stream of ozonized air, the compound is reacted with the ozonized air stream in the presence of an excess of the unsaturated hydrocarbon, cyclohexene. The oxygen content of the effluent from the mixture is measured over a course of time.

The character of the curve resulting from the plot of oxygen content versus time indicates to what degree the compound reacts preferentially with ozone in the presence of an unsaturated hydrocarbon. The real antiozonant value of compounds that can successfully compete for ozone in this test, however, must still be determined by testing the compound in a rubber recipe under conditions to be met in service.

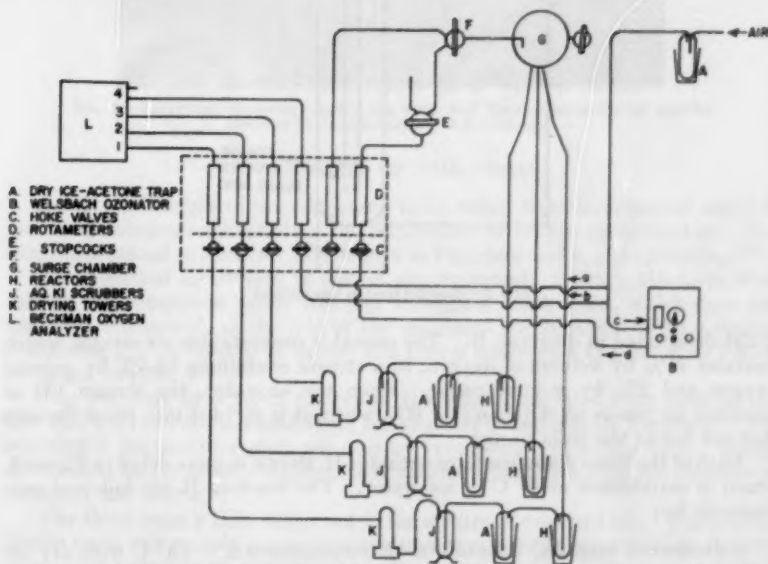


Fig. 2.—Schematic diagram of the equipment used for this screening method for selecting antiozonants.

DESCRIPTION OF THE APPARATUS

Figure 2 shows a schematic diagram of the ozonation train. Breathing air is led from a cylinder at 10 psig through an acetone dry ice trap, A, and is divided into three streams. Stream (a) passes through one of the rotameters D to the manifold G (surge chamber). This stream is used for flushing the apparatus with air. The second air stream (b) passes through a rotameter to the Beckman oxygen analyzer¹³, L. This stream is used to calibrate the oxygen analyzer. The third air stream (c) flows into the Welsbach ozonator¹⁴ (Model

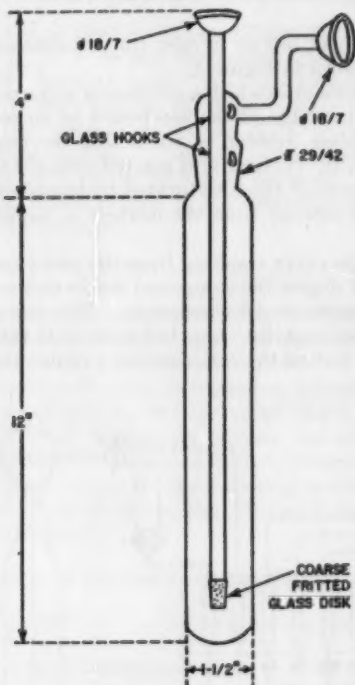


FIG. 3.—Reactor used in this method.

T-23) designated in diagram, B. The ozonator converts this air stream, which contains 21% by volume of oxygen, to a stream containing 18.5% by volume oxygen and 2% by volume ozone. From the ozonator, the stream (d) of ozonized air passes to the manifold (G), where it is divided into three streams that are fed to the train proper.

Each of the three trains contains a reactor H, shown in more detail in Figure 3, which is maintained at 0° C in ice water. The reactors H are followed successively by:

A freeze-out trap (A) maintained at temperatures of -78° C with dry ice and acetone.

A KI scrubber (J) containing 4% aqueous KI maintained at room tempera-

ture (the scrubber removes residual ozone from the stream to protect the oxygen analyzer.)

A drying tower (K) of anhydrous CaSO_4 .

The stream in each of the three trains passes through its separate rotameter (D) to the oxygen analyzer. By adjusting the rotameters, an even rate of flow for each stream through its train can be maintained. A picture of the assembly is shown in Figure 4.

The Beckman oxygen analyzer, Model F-3, with Speedomax¹⁵ recorder is used to determine the per cent by volume of oxygen in the streams from each of the three trains. Each stream is analyzed separately at ten-minute intervals. The oxygen analyzer is calibrated by means of the air stream (b) to record in the range 16–21% by volume of oxygen with an accuracy of $\pm 0.02\%$.



FIG. 4.—Laboratory equipment used in this work, with the reactors at the left and the ozonator at the right under the hooded area.

OPERATION OF THE TRAIN

A 0.01-mol sample of the compound to be tested as an antiozonant and 0.5-mol of cyclohexene are dissolved in 75 milliliters of carbon tetrachloride. The solution is placed in a reactor (H), shown in Figures 2 and 3, and chilled to 0°C .

The ozonized air stream is passed simultaneously through the train containing the compound under test and through a blank train, which does not contain a compound, at the rate of 140 milliliters per minute. With a stream containing 2% by volume of ozone, this rate is equivalent to 1.34×10^{-4} mols of O_3 per minute.

The per cent by volume oxygen of the effluent streams from each of the two trains is recorded alternately on the analyzer at ten-minute intervals. The recorder of the analyzer plots per cent by volume oxygen versus time. About 40–50 minutes are usually required to obtain sufficient data from the recorder to interpret the results.

The third train is then subjected to the stream of ozonized air. The reactor of this train will contain a second compound or possibly a check run on the first compound tested as an antiozonant. In general, the assembly runs smoothly with only an occasional, minor adjustment of the flow rates, which permits the

operator to recharge another reactor. Because of such continuous operation, five or six compounds may be evaluated per day.

INTERPRETATION OF RESULTS

Figure 5 is a simulated plot of the oxygen analyzer curves from the Speedomax recorder in which the time in minutes as abscissa is plotted against decrease of the per cent oxygen by volume as ordinate. The value of the air stream, 21% by volume oxygen, is the zero point on the ordinate.

The effluent from the blank KI-train gives a flat curve that indicates steady concentration of 20.2% by volume oxygen during the run, a decrease of 0.8% by volume in comparison to the oxygen content of the air stream.

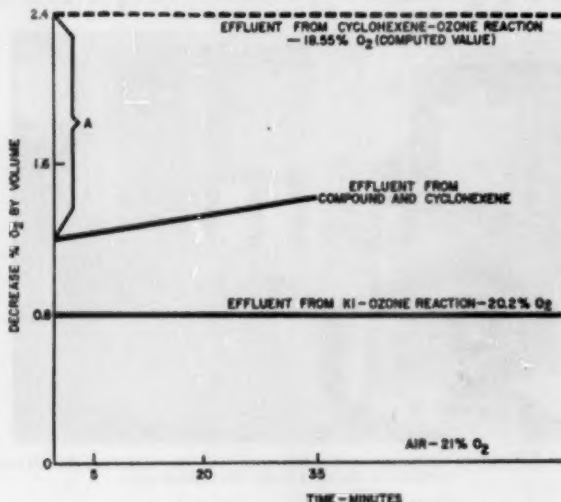


Fig. 5.—Simulated plot of the oxygen analyzer data.

Since the amount of ozone consumed by cyclohexene is three times the amount consumed by potassium iodide as shown in Equations 1 and 2, it is unnecessary to determine this curve. It can be plotted by computation.

The effluent stream from the reactor containing the mixture of compound and cyclohexene shows a progressive decrease in oxygen content in the course of time when the compound is sufficiently active to compete successfully with the large excess (50:1) of cyclohexene present in the mixture. The slope of this line will vary with the activity of the compound.

The intercept of this line on the ordinate at zero time, which is determined by extrapolation, is used in evaluating the compound. As shown in the figure, this intercept is at a distance "A" from the intercept of the cyclohexene effluent. The magnitude of "A" may be used to assign numerical values to a series of compounds to gage their potential value as antiozonants.

A known commercial antiozonant, N,N'-diethylparaphenylenediamine, is used as the standard for comparison in the method. Table I illustrates the duplicability of results for determining the "A" value for the reference compound. The figures in the "one-atom reaction" column are the values taken

by reading at zero time the intercept value of the oxygen analyzer curve for the effluent from the blank KI-train on the decrease of the per cent by volume oxygen ordinate. These values, which are read as a decrease in per cent by volume of oxygen from the unozone air stream, range from 0.88 to 0.94 for minor fluctuations in ozone content of the ozonized air stream.

TABLE 1

N, N'-DI-OCTYL-PARAPHENYLENEDIAMINE

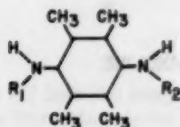
DECREASE % O₂ BY VOLUME

One-Atom Reaction	Three-Atom Reaction	Mixture	A
0.88	2.64	1.30	1.34
0.92	2.76	1.40	1.36
0.94	2.82	1.47	1.35
0.92	2.76	1.42	1.34
0.94	2.82	1.48	1.34

Experimental Error: $\pm 0.02\%$ by volume.

TABLE 3

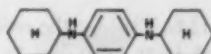
DERIVATIVES OF DIAMINODURENE



R ₁	R ₂	Comparative Reactivity
H	H	102
Isopropyl	H	95
2-Octyl	H	80
2-Octyl	2-Octyl	65
Isopropyl	Isopropyl	40

Reference Compound 100

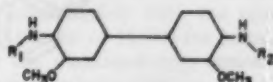
TABLE 2

DERIVATIVES OF
N, N'-DICYCLOHEXYL-PARAPHENYLENEDIAMINE

Reference Compound	Comparative Reactivity
N, N'-Dicyclohexyl	100
N, N'-Bis(3-methylcyclohexyl)	97
N, N'-Bis(4-methylcyclohexyl)	89
N, N'-Bis(3,3,5-trimethylcyclohexyl)	73
N, N'-Dicyclohexyl-N-2-hydroxyethyl	100
N, N'-Bis(2-hydroxyethyl)-N, N'-dicyclohexyl	101

TABLE 4

DERIVATIVES OF DIANISIDINE



R ₁	R ₂	Comparative Reactivity
2-Butyl	2-Butyl	101
Isopropyl	Isopropyl	98
Cyclohexyl	Cyclohexyl	95

Reference Compound 100

The values in the second column are those for the "three-atom reaction" and are computed by multiplying the values in the first column by three. They are values for the decrease in per cent by volume oxygen for the effluent from the reaction of the ozonized air stream with cyclohexene.

The third column lists the values for the decrease in per cent by volume oxygen for the effluent from the mixture of 0.01 mol of N, N'-diocetylparaphenylenediamine and 0.5 mol of cyclohexene dissolved in carbon tetrachloride. These values are taken from the intercepts of the effluent oxygen analyzer curves for this solution on the decrease in the per cent by volume oxygen ordinate at zero time.

The "A" values in the last column are computed by subtracting the values in the third column from those in the second column.

In the following tables showing the comparative reactivity of some of the compounds tested, the ratio of the experimentally determined "A" value for the compound under test to the experimental value of the reference compound, 1.35, is multiplied by 100 to obtain larger whole numbers.

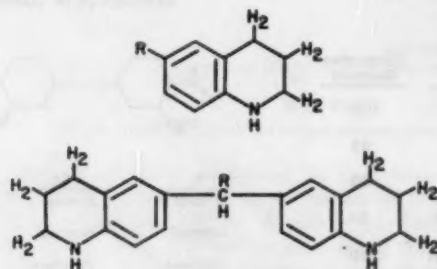
$$\text{Comparative Reactivity} = \frac{\text{"A"}}{1.35} \times 100$$

DISCUSSION OF RESULTS

Tables II to VI show the results obtained by this method on a series of compounds that have activities in the range of the reference compound, N,N'-dioctylparaphenylenediamine. Table II shows the comparative reactivities of a series of derivatives of N,N'-dicyclohexylparaphenylenediamine. Four of these derivatives show activities comparable to that of the reference compound. Decrease in activity with an increase in the number of methyl substituents on the cyclohexene ring is evident in the case of N,N'-bis(3,5,5-trimethylcyclohexyl)paraphenylenediamine.

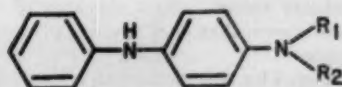
The last two derivatives are examples of the effect of introducing a third substituent, the hydroxyethyl group, into the molecule. No sacrifice in activity occurs by this modification. There is effected a marked decrease in the volatility of this product compared to the starting material. All of these compounds are crystalline solids.

TABLE 5
DERIVATIVES OF 1,2,3,4-TETRAHYDROQUINOLINE



Reference Compound	Comparative Reactivity
1,2,3,4-Tetrahydroquinoline	100
6-Methyl-1,2,3,4-tetrahydroquinoline	77
6-Cyclohexenyl-1,2,3,4-tetrahydroquinoline	110
1,1',2,2',3,3',4,4'-Octahydro-6,6'-biquinoline	96
6,6'-Cyclohexylidenebis (1,2,3,4-tetrahydroquinoline)	105
6,6'-Methylenebis (1,2,3,4-tetrahydroquinoline)	110
	103

TABLE 6
DERIVATIVES OF
N-PHENYLPARAPHENYLENEDIAMINE



R_1	R_2	Comparative Reactivity
H	Cyclohexyl	98
H	2-Octyl	90
Ethyl	Ethyl	86
H	3-(5-Methylheptyl)	81
H	2-Butyl	75
H	Isopropyl	75

Reference Compound 100

Table III lists the comparative reactivities of derivatives of diaminodurene. This is an interesting series in view of the findings reported by Andrews, quoted by Bailey¹⁰. In this work, the bimolecular rate constant for the ozonisation of methylated benzenes was found to increase considerably with the number of methyl groups on the ring and to reach a maximum of 15,000 for hexamethylbenzene compared to 1.9 for benzene. In the diaminodurene series shown, activity was found to decrease with increasing substitution on the nitrogen atoms with the least activity shown by the N,N'-disubstituted derivatives.

Three derivatives of dianisidine whose reactivity is comparable to the reference compound are shown in Table IV. These compounds are crystalline solids.

A number of derivatives of quinoline have been evaluated by our method. A selection from this collection is shown in Table V. Examples of two classes, both derived from 1,2,3,4-tetrahydroquinoline, were chosen. The 6-methyl and 6-cyclohexenyl derivatives, compared to the unsubstituted 1,2,3,4-tetrahydroquinoline, show enhanced activity. The second class is representative of higher molecular weight derivatives of 1,2,3,4-tetrahydroquinoline joined in the 6,6'-positions which show activities comparable to those of the reference compound.

Table VI shows a series of compounds derived from N-phenylparaphenylenediamine.

LIMITATIONS OF THE METHOD

Carbon tetrachloride has been found to be an acceptable solvent for the method. It is relatively inert toward ozone and readily available in a high state of purity. In working with this solvent, we have found that there is a very

slow, but nevertheless perceptible, reaction of spectrograde carbon tetrachloride with ozone at 0° C. In the course of an exposure of 50 min to 2% by volume of ozone, however, this reaction did not alter our results.

Compounds that will not dissolve in carbon tetrachloride at a concentration of 0.01 mol per 75 milliliters of 0° C in the presence of 0.5 mol of cyclohexene are discarded. Solubility of the compound in carbon tetrachloride alone is also used as a preliminary screen. Spot checking of carbon tetrachloride insoluble compounds has shown that they are usually too insoluble in rubber to perform as antiozonants.

Some compounds tested by this method have not given smooth plots on the oxygen analyzer that permitted extrapolation of the curve to zero time. These have been relatively few. Most organic compounds give smooth plots that fall within the area of the three-atom and one-atom reaction curves.

In a few instances curves with extremely steep slopes have been encountered. This result indicates ozone-catalyzed oxidation of the compound by the oxygen in the ozonized air stream. In these cases competition by the compound with the cyclohexene for the ozone in the stream is short-lived. The indicated potential antiozonant activity of the materials producing these curves, therefore is little.

SUMMARY AND CONCLUSIONS

A method has been developed for screening compounds for potential antiozonant use based upon the ability of the compound to suppress the reaction of ozone with cyclohexene when a mixture of the two is subjected to the action of a stream of ozonized air. The method is satisfactory as a tool for selecting compounds for testing in rubber.

In a rubber formulation, however, there are many factors concerned with the functioning of a compound as an antiozonant in addition to its ability to react preferentially with ozone at a faster rate than the unsaturated linkages in the rubber¹². Testing the most promising compounds in a rubber formulation is required to establish their commercial value as antiozonants.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Biggs, B. S., *RUBBER CHEM. & TECHNOL.* **31**, 1015 (1958).
- ² Long, L., Jr., *Chem. Rev.* **27**, 437 (1940).
- ³ Bailey, P. S., *Chem. Rev.* **58**, 925 (1958).
- ⁴ Barnard, D., *J. Chem. Soc.* 4547 (1947).
- ⁵ Delman, A. D., Simons, B. B., and Allison, A. R., *Anal. Chem.* **26**, 1589 (1954).
- ⁶ Neresheimer, H., *Rev.* **39**, 2848 (1906).
- ⁷ Harries, C. and Seitz, R., *Ann. Chem.* **410**, 25 (1915).
- ⁸ Criegee, R., Blust, G., and Lohaus, G., *Ann.* **583**, 2 (1953).
- ⁹ Mensies, R. C., and Robinson, R., *J. Chem. Soc.* **125**, 2136 (1924).
- ¹⁰ Bailey, P. S., *J. Org. Chem.* **22**, 1548 (1957).
- ¹¹ Thorp, C. E., "Bibliography of Ozone Technology", Vol. 1, pp. 39-58. Armour Research Foundation, Illinois Institute of Technology, Chicago, Ill.
- ¹² Shaw, R. F., Ossefort, Z. T., and Touhey, W. J., *Rubber World* **130**, 636 (1954).
- ¹³ Arnold O. Beckman, Inc., South Pasadena, Calif.
- ¹⁴ The Weisbach Corp., Philadelphia, Pa.
- ¹⁵ Leeds & Northrup Co., Philadelphia, Pa.

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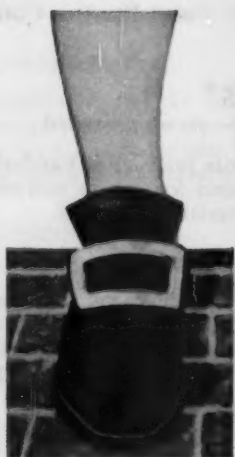


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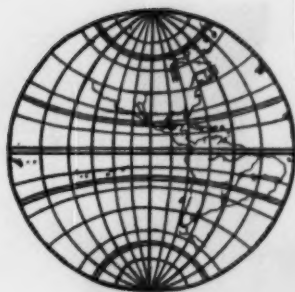
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organic material. They disperse in a rubber mix rapidly and thoroughly, developing physical properties, in vulcanized rubber comparable to standard Black Label No. 20 and Green Label No. 42.

GREEN LABEL No. 46

Low pH type used in foam latex where zinc oxide is used for both activation and as a supplementary gelling agent.

RED LABEL No. 30

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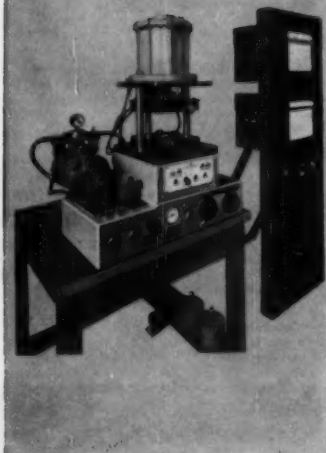
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